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THE UNIVERSITY OF ALBERTA

STRUCTURAL AND CHEMICAL INVESTIGATIONS
OF ARYLDIAZONIUM AND DIAZOALKANE SPECIES

by



Michele Dorothy Gauthier

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE

IN

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

FALL, 1980

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies and Research,
for acceptance, a thesis entitled STRUCTURAL AND CHEMICAL
.....
INVESTIGATIONS OF ARYLDIAZONIUM AND DIAZOALKANE SPECIES
.....
submitted by Michele Dorothy Gauthier in partial
.....
fulfilment of the requirements for the degree of Master
of Science in Chemistry.

To Miles
and my Family

ABSTRACT

The X-ray structural determination of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{NH}_2\text{NPh})][\text{BF}_4]$, ($\text{Ph} = (\text{C}_6\text{H}_5)$), has indicated that the coordination about the W atom is pseudotetrahedral, with two of the coordination sites occupied by the cyclopentadienyl rings, and two by the novel side-on bonded phenylhydrazido-(1-) ligand. This unusual ligand has resulted from the insertion of $(\text{C}_6\text{H}_5)\text{N}_2^+$ into both W-H bonds of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{WH}_2]$. The two W-N bond lengths are inequivalent (2.156(9) and 2.034(9) Å), with the shorter distance corresponding to the three-coordinate nitrogen atom, which is bonded to the phenyl group. The N-N distance (1.43(1) Å) corresponds to a normal N-N single bond.

Two diazoalkane molecules, $(\text{PhCO})_2\text{CN}_2$ and PhCOCN_2Ph have been structurally characterized. The former, dibenzoyldiazomethane, was found to have an s-trans-s-cis geometry of the carbonyl and diazo groups about the C-C single bonds. This molecule is non-planar, although the structural parameters ($\text{N-N} = 1.112(2)$ Å, $\text{C-N} = 1.339(2)$ Å, $\text{C-O} = 1.224(2)$ and $1.221(2)$ Å) indicate a significant amount of π -delocalization between the two carbonyl groups and the diazomethane moiety. The carbonyl and diazo groups in the second diazoalkane compound, benzoylphenyldiazomethane, are trans to each, and the molecule, again, is non-planar. As was the case for $(\text{PhCO})_2\text{CN}_2$, there is a significant amount of π -delocalization between the carbonyl and diazo groups,

(N-N=1.130(5)Å, C-N=1.328(5)Å, C-O=1.231(4)Å), although there is little conjugation between the phenyl rings and these two groups.

The chemistry of one of the diazoalkane molecules, dibenzoyldiazomethane, with several Rh and Ir complexes has been investigated. In the reaction of $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ and $((\text{C}_6\text{H}_5)\text{CO})_2\text{CN}_2$, several species were formed, of which only one compound was characterized - $[\text{IrCl}\{(\text{OCPh})_2\text{CN}_2\}(\text{PPh}_3)_2]$, in which the diazoalkane molecule is chelated through the two ketonic oxygen atoms. No reaction occurred between $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ and dibenzoyldiazomethane. The reaction of the diazoalkane and $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ and PPh_3 resulted in the formation of several species, and one of these, $[\text{IrCl}((\text{C}_6\text{H}_4)\text{COCC}(\text{Ph})\text{OPPh}_2)(\text{PPh}_3)_2]$ was structurally characterized. This complex was found to contain the unusual tridentate ligand, $((\text{C}_6\text{H}_4)\text{COCC}(\text{Ph})\text{OPPh}_2)$, which is coordinated to the metal through an orthometallated phenyl ring, a vinylic carbon atom and a phosphorus atom, and has been formed through the condensation of the carbene fragment $(\text{PhCO})_2\text{C}$ and a diphenylphosphine group. In an analogous reaction between $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$, $(\text{P}(i\text{-C}_3\text{H}_7)_3)$ and $(\text{PhCO})_2\text{CN}_2$, the phosphazine $(i\text{-C}_3\text{H}_7)_3\text{P}=\text{N}_2\text{C}(\text{COPh})_2$ was the only product detected, while the reaction of $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$, PPh_3 and the diazoalkane produced two products: a phosphazine, $\text{Ph}_3\text{P}=\text{N}_2\text{C}(\text{COPh})_2$, and a phosphorus ylide, $\text{Ph}_3\text{P}=\text{C}(\text{COPh})_2$. If a mixture of $[\text{RhCl}(\text{PPh}_3)_3]$ and $[\text{RhCl}(\text{PPh}_3)_2]_2$ were reacted with dibenzoyldiazomethane, only the former reacted, producing the phosphorus ylide, $\text{Ph}_3\text{P}=\text{C}(\text{COPh})_2$.

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Dr. Larry Vande Griende, for preparing the sample of $\text{Ph}_3\text{P}=\text{C}(\text{COPh})_2$;

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ABBREVIATIONS

Ar = aryl

Me = methyl

Ph = phenyl

L = ligand

Et = ethyl

bipy = 2,2'-bipyridine

PPP = $[\text{Ph}_2\text{P}(\text{CH}_2)_3]\text{PPh}$

Cy = cyclohexyl

DPM = bis(diphenylphosphino)methane

Bu = butyl

Cp = cyclopentadienyl

CR = centre of ring

CR1 = centre of ring 1

CR2 = centre of ring 2

THF = tetrahydrofuran

Chapter I.

INTRODUCTION

The transition metal chemistry of two closely related species, the aryldiazonium cation (N_2Ar^+) and the diazoalkane molecule (N_2CRR') have been the subject of much interest in recent years.^{1,2} Metal complexes of the former species have been used as model systems for the study of nitrogen fixation, whereas the importance of diazoalkane compounds has resulted from their synthetic utility in organometallic chemistry.

Metal-aryldiazonium complexes have been studied in relation to nitrogen fixation, the process in which dinitrogen is reduced to ammonia.³ Commercially, this process is a key step in the manufacture of plastics and fertilizers, but requires high temperatures and pressures. In nature however, nitrogen fixation is catalyzed in some plants under ambient conditions by nitrogenase, an enzyme containing molybdenum and iron.⁴ The industrial importance of an easily synthesized catalyst which could mimic the action of nitrogenase is obvious, and much work is currently underway in attempts to produce such a species. Researchers have used various metal complexes as model systems in these studies, in particular metal-dinitrogen complexes⁵ and metal compounds with dinitrogen-containing

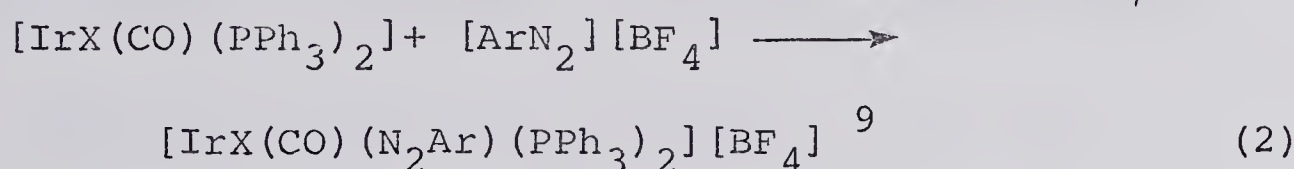
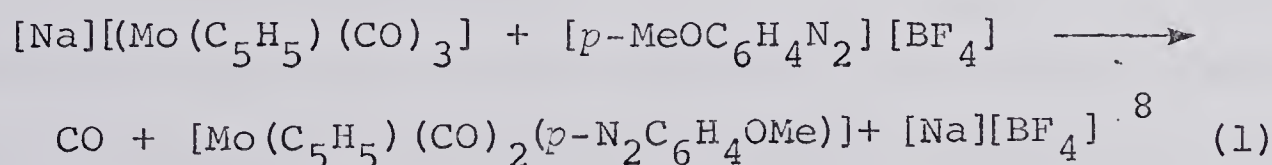
ligands.⁶ One prime example of the latter is the aryldiazonium cation.

Interest in diazoalkane molecules, on the other hand, has mainly been as a result of their versatility as reagents in the preparative chemistry of transition metal complexes,² since a wide variety of metal complexes are formed from aliphatic diazo compounds. Some of these complexes contain the intact diazoalkane molecule, while others contain fragments of the diazoalkane molecule, either intact or rearranged. The complexes formed include alkyl, olefin, acetylene, carbene, ketene, μ -methylene, μ -methylidene, alkylazo, ketenimine and ketazine metal species.² The mechanisms for many of the reactions producing these species are unknown and are under investigation.² The transition metal coordination of diazoalkane molecules is also relevant to studies involving metal coordinated olefins. Although these latter species have been widely studied in organometallic chemistry,⁷ especially in relation to catalysis, the related diazoalkane species containing C=N or N=N bonds are much more uncommon.

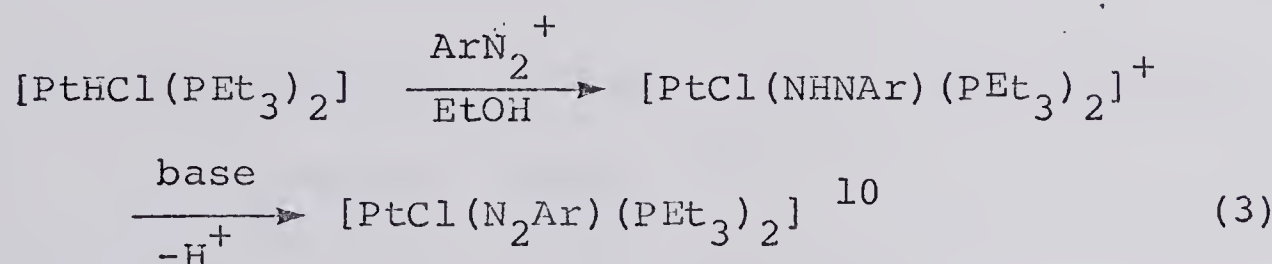
In studying the chemistry of transition metal complexes with aryldiazonium and diazoalkane molecules, it is necessary to understand not only the synthetic reactions leading to metal-coordinated species but also the structural details of these species, and their subsequent reactions. There has been a considerable amount of work done in each of

these areas already, and the results to date are briefly presented below.

Metal-diazonium complexes have been synthesized through two major routes,¹ either directly by the reaction of a diazonium salt with a metal compound or indirectly through the reaction of various organic molecules (such as arylhydrazines or diazenes) with metal species. In the direct reactions with diazonium salts, metal-coordinated compounds have been formed through substitution, oxidative addition or insertion reactions followed by deprotonation, as illustrated in equations (1), (2) and (3), respectively.



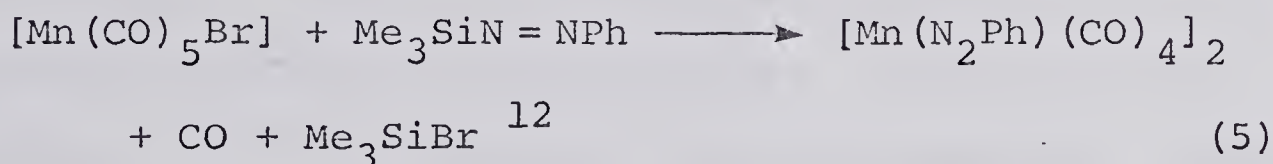
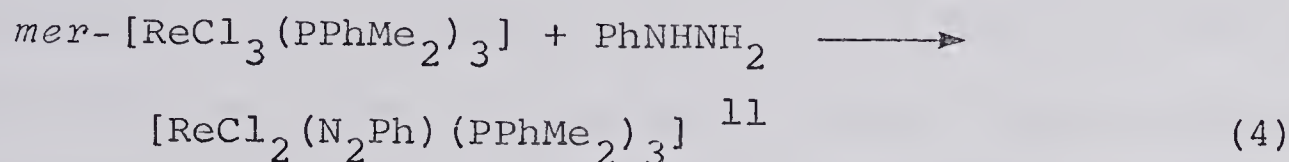
X = Cl, Br



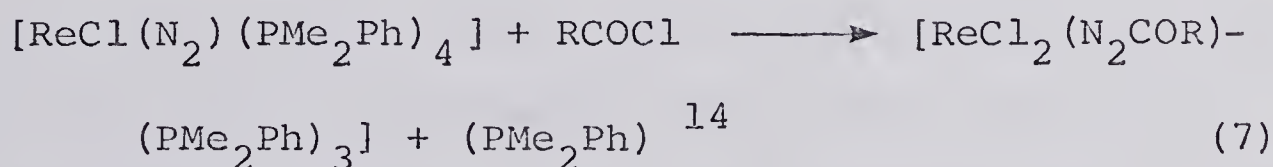
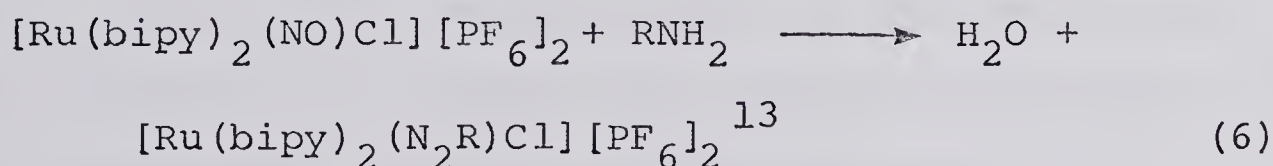
Although these direct reactions are straight forward in principle, they are often quite complex, and cannot always be used in the preparation of diazonium complexes. In equation (2), for example, in addition to the product shown,

an orthometallated species $[\text{Ir}(\text{NHNHAr})(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$, a diaryltetrazenido complex $[\text{Ir}(\text{N}_4\text{Ar}_2)(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ and an orthometallated aryldiazene complex $[\text{IrCl}(\text{NHNAr})(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ were also obtained and characterized.⁹

In the indirect syntheses of metal diazonium complexes, both arylhydrazines (Equation (4)) and aryldiazenes (Equation (5)) have been used.



In addition, metal nitrosyl and metal dinitrogen complexes have been reacted with organic molecules to produce diazonium complexes (Equations (6) and (7), respectively).



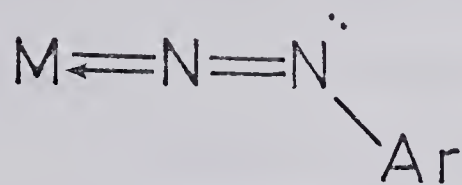
Metal dinitrogen complexes also form diazonium complexes under irradiation in the presence of XR, where X = Cl, Br, I and R = Me, xylene, cyclohexane or ethylformate.¹⁵

In a reaction with a metal complex, the diazonium ion usually acts as an electrophile through the terminal nitro-

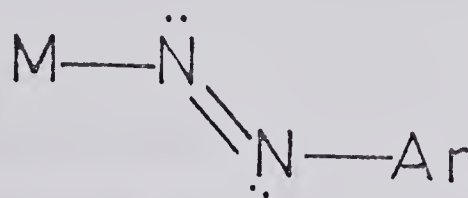
gen atom.¹⁶ Once coordinated, this ligand can display a variety of coordination modes, as shown in Figure 1. The diazonium ion can be terminally bound to one metal centre, or bridging two or more metals. If bound to one metal, the aryldiazonium ligand can act formally as a three-electron donor, or as a one-electron donor. In the former mode, one would expect a linear M-N-N fragment and an NNC angle of approximately 120° (Structure 1a). The ligand in this case is described as being "singly bent" and is formally considered as ArN_2^+ .¹ Several such complexes have been synthesized and structurally characterized. In $[\text{Re}(\text{N}_2\text{Ph})\text{Cl}_2(\text{PMe}_2\text{Ph})_3]$,^{11,17} for example, the M-N-N angle was found to be 173(2)°, while the N-N-C angle was 119(2)°, in agreement with the predicted values. In addition, both the M-N and the N-N bond lengths indicate double bond character (1.77(2) and 1.23(2) Å, respectively), while the N-C bond length (1.43(2) Å) is typical for a single bond between these atoms, as expected for this coordination mode.

As a one-electron donor, the aryldiazonium ligand is doubly bent, with approximately 120° angles about both nitrogen atoms. In this case, the ligand can adopt a trans or cis configuration, as illustrated in Figures 1b and 1c, and is considered formally as ArN_2^- . Three structures have been determined of doubly bent aryldiazonium complexes,^{9,18,19} and all have had the trans geometry. A typical example is $[\text{Rh}(\text{N}_2\text{Ph})\text{Cl}(\text{PPP})]^+$,¹⁸ which has an M-N-N angle

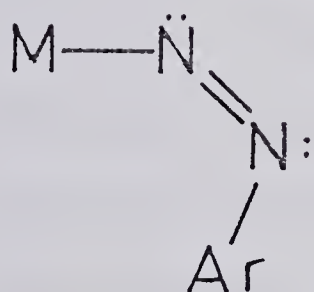
Figure 1. Bonding Modes in Metal-Aryldiazonium Complexes.



a



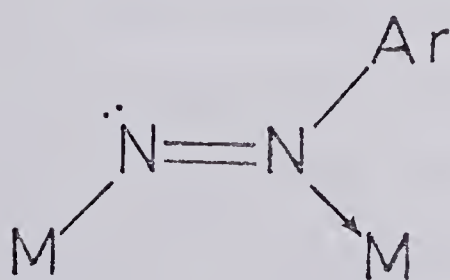
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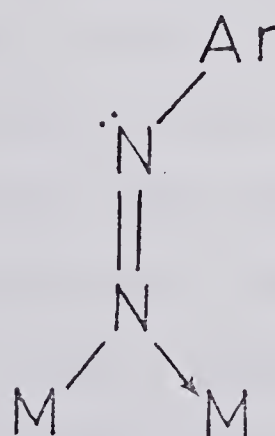
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d



e



f

of $125.1(6)^\circ$ and an N-N-C angle of $118.9(8)^\circ$. The M-N bond length ($1.961(7)\text{\AA}$) is considerably longer than in the singly bent Re complex (described above). The N-N bond length ($1.172(9)\text{\AA}$) and the N-C bond length ($1.445(11)\text{\AA}$) are in keeping with the double and single bonds expected, respectively, for this geometry.

A complex containing a diazonium ligand with an intermediate geometry, $[\text{IrCl}(\text{N}_2\text{Ph})(\text{P}(\text{CH}_3)(\text{Ph}_2))_3][\text{PF}_6]$, has been reported by Cowie, Haymore and Ibers.²⁰ In this species the unusual intermediate geometry is attributed to steric crowding about the metal centre, which forces the N_2Ph ligand into the "half doubly bent" configuration. The structural parameters of this ligand confirm the intermediate geometry. Therefore, the M-N-N angle of $155.2(7)^\circ$ and the M-N bond length ($1.835(8)\text{\AA}$) are intermediate between values reported for the singly bent and doubly bent structures. The diazonium ion can be considered as a 2-electron donor in this complex.

The totally linear geometry, as in Figure 1d, has never been structurally characterized although its existence has been postulated for $[\text{RhCl}(\text{N}_2\text{Ph})(\text{PPh}_3)_2][\text{PF}_6]$ and $[\text{RhCl}(\text{N}_2\text{Ph})(\text{CO})(\text{PCy}_3)_2]$, where unusually high values of ν_{NN} (1980 and 2000 cm^{-1} , respectively) were observed.²¹ The difference between a totally linear configuration and a singly bent geometry is dependent upon the extent of back donation from the metal atom to the diazon-

ium ligand, since very little back donation is expected for the former, and substantial back donation is required for the singly bent geometry.¹ Intermediate back donation from the metal will result in N-N-C angles between the extremes of 120 and 180°, as was observed in $[\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2]$, where the N-N-C angle is 137.1(5)°. ²²

In addition to bonding through the terminal nitrogen atom to one metal centre, the diazonium ligand can also bridge two metals. Of the two possible geometries shown in Figures 1e and 1f, only the latter has been observed, and three such structures are known, $[\text{Pd}_2\text{Cl}_2(\mu\text{-N}_2\text{Ph})(\text{DPM})_2]^+$, ²³ $[\text{Ir}_2(\mu\text{-O})(\mu\text{-N}_2\text{C}_6\text{H}_4(2\text{-NO}))(\text{NO})_2(\text{PPh}_3)_2]^- [\text{PF}_6]^{24}$ and $[\text{Mn}(\text{CO})_4(\mu\text{-N}_2\text{Ph})]_2$. ¹² The Mn compound has two bridging diazonium groups, which display similar bonding parameters. Within each ligand, the two M-N bond lengths are virtually identical (2.031(2) and 2.021(2) Å) indicating that the three electrons donated by the diazonium group are equally shared by the two metal centres. The N-N-C bond angle is 119.7(2)°, while the N-N bond length of 1.234(3) Å indicates a double bond and the N-C bond length (1.445(3) Å) is characteristic of a single bond.

Once a metal-diazonium complex is formed, it can undergo a variety of further reactions. Of particular interest to the nitrogen fixation studies, are the protonation reactions of these complexes. In a singly bent aryldiazonium compound, the second nitrogen atom is most likely to be

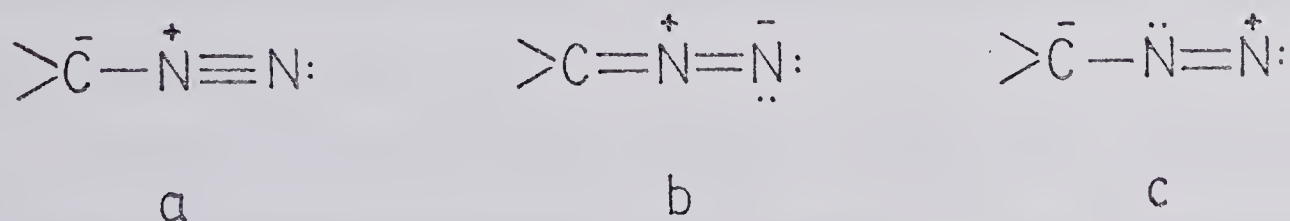
protonated, as was observed for $[\text{ReCl}_2(\text{NNHPh})(\text{PMe}_2\text{Ph})_2^-(\text{NH}_3)]^+$.¹⁷ On the other hand, with doubly bent aryldiazonium complexes, the site of protonation is the first nitrogen atom, which is bound to the metal. An example of this is the reversible reaction of $[\text{Pt}(\text{N}_2\text{C}_6\text{H}_4\text{X})(\text{PPh}_3)_3]\text{Y}$ ²⁵ ($\text{X} = p\text{-NO}_2, \text{F}, \text{H}, \text{OMe}, \text{Me}, \text{NEt}_2$ or NMe_2 ; $\text{Y} = \text{BF}_4$ or BPh_4) with non-coordinating acids to yield $[\text{Pt}(\text{NHNC}_6\text{H}_4\text{X})(\text{PPh}_3)_3]^{2+}$.

Hydrogenation studies on metal-diazonium complexes have also been investigated.²⁶ Singly bent diazonium complexes are not usually hydrogenated under mild conditions,²⁶ but several doubly bent aryldiazonium species have been hydrogenated under mild conditions in the presence of a catalyst to yield hydrazine complexes ($\text{M-NH}_2\text{NHAr}$).²⁶ Doubly bent aryl-diazonium complexes, already protonated on the first nitrogen atom, also react with H_2 to form metal hydrazines.²⁶ In addition, orthometallated aryldiazonium complexes are readily hydrogenated under mild catalytic conditions, yielding orthometallated arylhydrazine species.²⁶ In contrast, it has been reported²⁵ that $[\text{Pt}(\text{N}_2\text{C}_6\text{H}_4\text{X})(\text{PPh}_3)_3]^+$ complexes ($\text{X} = p\text{-NO}, \text{F}, \text{H}, \text{OMe}, \text{Me}, \text{NEt}_2$ or NMe_2) react with H_2 in the absence of a catalyst to produce only N_2 and $[\text{PtH}(\text{PPh}_3)_3]^+$; no intermediate aryl-diazine or hydrazine complexes were observed.

Metal-aryldiazonium complexes may also undergo orthometallation, displacement or oxidative addition reactions. Orthometallation of the aryl group has been observed upon refluxing²⁷ or if an α -hydridic alcohol, such as ethanol,

is present.¹ In displacement reactions, either the aryl-diazonium ligand or another ligand within the complex may be displaced. The former has been observed in the reaction of $[\text{Os}(\text{CO})_2(\text{NNPh})(\text{PPh}_3)_2]^+$ with BH_4^- yielding $[\text{OsH}_2(\text{CO})_2^-(\text{PPh}_3)_2]$,²⁸ while an example of displacement of another ligand occurs in the reaction of $[\text{PtCl}(\text{N}_2\text{Ar})(\text{PEt}_3)_2]$ with L ($\text{L} = \text{NH}_3$, pyridine, PEt_3 , EtNC) producing $[\text{PtL}(\text{N}_2\text{Ar})(\text{PEt}_3)_2]^+$, an unstable complex which subsequently decomposes to $[\text{PtL}(\text{Ar})(\text{PEt}_3)_2]^+$ and N_2 .²⁹ Oxidative addition reactions have also been noted for several metal-aryldiazonium complexes, as in the reaction of $[\text{IrCl}(\text{N}_2\text{Ar})(\text{PPh}_3)_2]^+$ with CO , PR_3 , AsR_3 , SbR_3 and RCN to form five coordinate species.³⁰

Unlike diazonium ions, neutral diazoalkane molecules rarely produce complexes containing the intact molecule in reactions with metal species.² This is a function of the electronic structure of diazoalkane molecules, which can be represented by three canonical forms,



The aliphatic diazo molecules can react as nucleophiles through either the carbon atom (a) or the terminal nitrogen (b); as a 1,3-dipole as in (c); or as a π -donor through either the C-N or N-N moieties.¹⁶ These reaction pathways lead to

three major classes of products: rearranged organic compounds, metal-carbene complexes and metal-diazoalkane complexes.

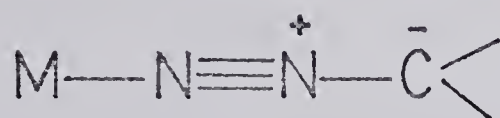
Various organic compounds have been produced from reactions between diazoalkane molecules and metal species. These include ketenes ($RR'C=C=O$), which have been formed either with an excess of $Ni(CO)_4$ ³¹ or with catalytic amounts of Cu powder or Ag compounds;³² methylene addition products, as in the formation of dicyclopropylmethane from $cis-(\eta^3\text{-allyl})_2Ni$;³³ polymethylene, produced from reactions between diazomethane and nickelocene³⁴ or $IrCl(CO)(PPh_3)_2$, (in $CHCl_3$ or benzene);³⁵ and ethylene, produced from diazomethane and $IrCl(CO)(PPh_3)_2$ in diethyl ether,³⁵ or $TiCl_4$.³⁶ Diazoalkanes have also been used in catalytic amounts as initiators in the WCl_6 -catalyzed olefin metathesis of cycloalkenes to polyalkenamers of high molecular weight.³⁷ For most of these products, the reaction mechanisms are not well understood, although it is postulated that primary adducts of the diazoalkane molecule and unstable carbene complexes are involved.²

Several metal-carbene products have been isolated from aliphatic diazo molecules. One example is $[(\eta^5\text{-C}_5\text{H}_4\text{R})Mn(CO)_2((C_6H_5)CCO(C_6H_5))]$, ($R = H, Me$) produced from the reaction of benzoylphenyldiazomethane and $[(\eta^5\text{-C}_5\text{H}_4\text{R})Mn(CO)_2(THF)]$.³⁸ This carbene complex produces the corresponding Mn-ketene complex $[(\eta^5\text{-C}_5\text{H}_4\text{R})Mn(CO)_2(Ph_2C=C=O)]$ under

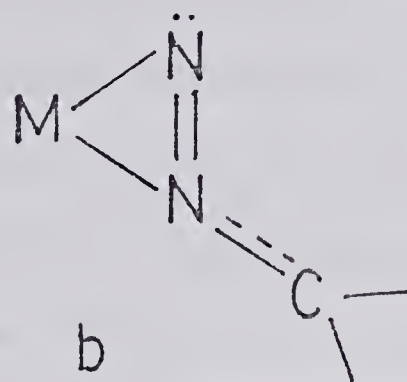
irradiation. Intramolecular rearrangements often occur with these metal carbene complexes. In the reaction of the above Mn-(THF) adduct with 3-diazo-2-butanone for example, the carbene complex cannot be isolated, and the resulting complex, $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mn}(\text{CO})_2(\text{H}_2\text{C}=\text{CHCOCH}_3)]$, an η^2 -bound olefin complex, is obtained instead.^{38b} Carbenes bridging two metal centres, μ -methylene complexes, have been reported for reactions between diazoalkanes and various metal species, including Mn, Os, Co and Rh.² A μ_3 -methylidene cluster was also noted from the reaction of diazomethane and $\text{H}_2\text{Os}_3(\text{CO})_{10}$.³⁹ Insertion of carbenes produced from aliphatic diazo molecules into metal hydrides has resulted in metal-alkyl compounds, as in the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{H}$ with diazomethane to produce $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CH}_3)(\text{CO})_3$.⁴⁰ Diazoalkane-produced carbenes have also inserted into M-C bonds, which in the reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{Ph-C}\equiv\text{C-Ph})(\text{PPh}_3)$ and $\text{N}_2\text{CH}(\text{CO}_2\text{CH}_3)$, resulted in the formation of three complexes - a mononuclear butadiene, and two bridging hexadiene species.⁴¹

Relatively few stable metal-diazoalkane complexes have been isolated. This is due mainly to the reactivity of these metal species, which usually results in further reactions and rearrangements (*vide supra*). Within a mononuclear diazoalkane complex, there are several possible bonding modes, and these are presented in Figure 2. In type 2a the diazoalkane molecule is coordinated through the terminal nitrogen atom, and has been observed for such complexes as

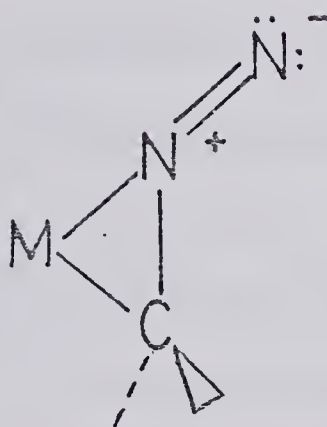
Figure 2. Bonding Modes in Mononuclear Metal-Diazoalkane Complexes.



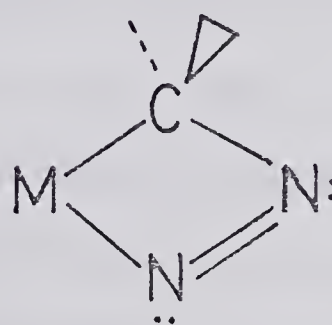
a



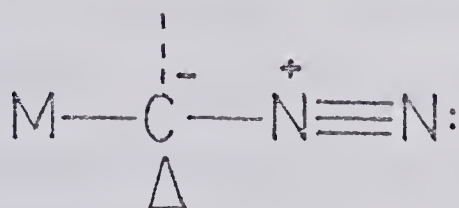
b



c



d



e

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{N}_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2)]$,⁴² $[\text{IrCl}(\text{N}_2\text{C}_5\text{Cl}_4)(\text{PPh}_3)_2]$ ⁴³
 and $[\text{RuH}_2(\text{N}_2\text{B}_{10}\text{H}_8\text{S}(\text{CH}_3)_2)(\text{PPh}_3)_3]$.⁴⁴ The latter two species have been confirmed by X-ray crystallography. In the iridium complex, the diazoalkane ligand is comparable to the singly bent aryldiazonium ligand in $[\text{IrCl}(\text{N}_2\text{Ph})(\text{PPh}_3)_2]^+$,³⁰ although the bonding parameters indicate that there is less π -back bonding from the metal to the ligand for the diazoalkane complex (diazoalkane[aryldiazonium] parameters:⁴³
 $\angle \text{Ir-N-N} = 174.6(6)^\circ [176.1^\circ]$, $\angle \text{N-N-C} = 141.2(7)^\circ [124.8^\circ]$,
 $\text{Ir-N} = 1.824(6)\text{\AA} [1.794\text{\AA}]$, $\text{N-N} = 1.163(7)\text{\AA} [1.159\text{\AA}]$). The above ruthenium-diazoalkane complex was found to be totally linear⁴⁴ with an M-N-N angle of $175.9(6)^\circ$ and an N-N-B angle of $172.7(8)^\circ$. Analogous linear aryldiazonium complexes have been proposed, although none has been structurally characterized. The Ru-N bond distance ($1.889(8)\text{\AA}$) and the N-N bond length ($1.115(8)\text{\AA}$) are comparable to those found in ruthenium-dinitrogen complexes.

Diazoalkane complexes coordinated through the N=N double bond (Figure 2b) have been isolated for various metal species, and one such complex, $[\text{Ni}(t\text{-BuNC})_2(\text{diazofluorene})]$ has been structurally characterized.⁴⁵ The diazoalkane ligand is bound unsymmetrically to the metal atom, with Ni-N distances of $1.874(3)$ and $1.834(3)\text{\AA}$. The N-N distance of $1.245(4)\text{\AA}$ is characteristic of an N=N double bond and the N-N-C bond angle is $133.8(3)^\circ$. Analogous π -coordinated aryldiazonium species have not been observed.

Other coordination modes have been postulated as intermediates in various reactions between metal complexes and diazoalkane molecules, but have not been fully characterized. For example, diazoalkane complexes which are π -coordinated through the N-C bond (Figure 2c) have not been isolated, but may be involved in reactions where the N-N bond is cleaved, as in the formation of ketimine complexes from diazoalkanes.⁴⁶ Four-membered metallocycles (Figure 2d) have been suggested as intermediates in the formation of carbene addition products,⁴⁷ and this coordination mode has been postulated for $[\text{IrCl}(\text{NNC}(\text{CF}_3)_2)(\text{PPh}_3)_2]$,⁴⁸ although this has not been confirmed through a structure analysis. Similarly, coordination through the aliphatic carbon atom of the diazoalkane, (Figure 2e) has been considered for primary adducts in several reactions, but compounds with this coordination mode have not been isolated.² On the other hand, the related species, containing a metallated diazoalkane, has been reported for several group IB⁴⁹ and IIB⁵⁰ transition metals, such as $\text{Hg}(\text{C}(\text{N}_2)\text{R})_2$. Metallated diazoalkane complexes of the group VIII transition metals such as $[\text{PdCl}(\text{C}(\text{N}_2)\text{R})(\text{PR}'_3)_2]$ and $[\text{Pd}(\text{C}(\text{N}_2)\text{R})_2(\text{PR}'_3)_2]$ have been prepared through the reaction of $\text{Hg}(\text{C}(\text{N}_2)\text{R})_2$ with $[\text{PdCl}_2(\text{PR}'_3)_2]$, where $\text{R} = \text{CO}_2\text{Et}$, $\text{C}(\text{O})\text{Me}$, Ph and $\text{R}' = \text{Ph}, \text{Et}$.⁵¹ The X-ray structure of one of the products, $[\text{PdCl}(\text{C}(\text{N}_2)\text{CO}_2\text{Et})(\text{PPh}_3)_2]$, confirmed the metallated configuration of the diazoalkane ligand.⁵¹

Metal diazoalkane complexes in which the aliphatic diazo ligand is coordinated to more than one metal centre are very rare. In one reported complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_3^{3-}(\mu_3\text{-CO})(\mu_3\text{-N}_2\text{CPh}_2)$,⁵² the diazoalkane is bridging three cobalt atoms through the terminal nitrogen atom. In $[\text{Mn}(\text{CO})_4]_3^{3-}(\mu_3\text{-N}_2\text{CH}_3)$ ⁵³ the terminal nitrogen atom is bound to two Mn atoms, while the other nitrogen atom is coordinated to the third Mn centre.

In some reactions, metal-nitrogen species are formed which are not diazoalkane complexes. An illustration of this are the alkyldiazo insertion products $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{N}_2\text{CHRR}')]]$ where $\text{M} = \text{Mo}, \text{W}$ and $\text{R}, \text{R}' = \text{H}, \text{CH}_3, \text{Si}(\text{CH}_3)_3, \text{C}_6\text{H}_5$, which are formed from the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}]$ and $\text{N}_2\text{CRR}'$.⁵⁴ Another example is the reaction of ethyldiazoacetate with $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ which produces the dinitrogen complexes $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ and $[(\text{NH}_3)_5\text{Ru}-(\text{N}_2)-\text{Ru}(\text{NH}_3)_5]^{4+}$.⁵⁵

Some further reactions have been reported for metal-diazoalkane complexes, however, the work done in this area has been limited since so few of the diazoalkane complexes are stable. Schramm and Ibers⁴³ reported that $[\text{IrCl}(\text{N}_2\text{C}_5\text{Cl}_4)(\text{PPh}_3)_2]$ oxidatively adds various molecules, such as PR_3 , CO , NO^+ and N_2Ph^+ , in a manner similar to the addition reactions of the corresponding aryldiazonium complex.³⁰ Differences however arise between the diazoalkane and aryldiazonium complexes, since the diazoalkane ligand is neutral whereas the diazonium ion is positively charged. Displacement reactions have also been observed with metal-

diazoalkane compounds. The π -coordinated diazofluorene molecule is displaced in the reaction of $[\text{Ni}(t\text{-BuNC})_2^- (\text{diazofluorene})]$ with PPh_3 , while in the analogous Pd complex, a $(t\text{-BuNC})$ group is displaced.⁴⁵ In addition, in virtually all metal-diazoalkane complexes, thermal decomposition readily occurs, with loss of the diazoalkane ligand.²

The chemistry of diazoalkane molecules with transition metal compounds is very complex, and a wide variety of species, both organic and organometallic, are obtained. This variety, in fact, is the basis for the synthetic utility of diazoalkane molecules in organometallic chemistry. As in the case of the diazonium ions, the mechanisms involved in these reactions are not well understood and there is still much work to be done in this area.

As can be seen, diazoalkane molecules and aryldiazonium ions are closely related, yet their reactions with transition metal compounds are quite different, as are the coordination modes and chemistry of the resultant complexes. This study was undertaken to further investigate the nature of aryldiazonium and diazoalkane transition metal complexes, with particular emphasis on the structural details of the complexes. The technique of X-ray diffraction was used extensively during this study and detailed discussions of the theoretical and experimental considerations of this technique are available in several reference texts.⁵⁶⁻⁵⁹

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Chapter II.

The Structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{H}_2\text{NNC}_6\text{H}_5)][\text{BF}_4]$:

A Complex Containing the Unusual Side-On

Bonded Phenylhydrazido(1-) Ligand.

INTRODUCTION

The insertion reactions of aryldiazonium cations into transition metal-hydride bonds have received much attention,¹⁻³ owing in part to the possible relevance of such studies to the biological reduction of dinitrogen, as initially suggested by Parshall.⁴ Although several examples of monoinsertion reactions, in which an aryldiazonium cation inserts into one metal hydride bond, have been characterized and reported,¹⁻³ the isolation and characterization of stable products resulting from the double insertion of N_2Ph^+ into two metal-hydride bonds had not been reported until recently.^{5,6} The hydrazido(1-) species resulting from this double insertion reaction represents an important intermediate in model system studies of dinitrogen reduction.

The reaction of Cp_2WH_2 with N_2Ph^+ at low temperature initially yields^{5,6} the monoinserted species, $[\text{Cp}_2\text{WH}(\text{NNHPh})]^+$, which has been shown to contain a hydrazido(2-) ligand, in which the hydrogen atom is bonded to the second nitrogen atom, remote from the metal.⁷ At room temperature this unstable intermediate rearranges to the diinserted

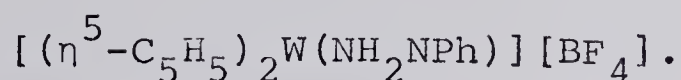
product, $[\text{Cp}_2\text{W}(\text{H}_2\text{NNPh})]^+$, which based on spectral measurements was believed to contain the novel side-on bonded phenylhydrazido(1-) ligand.^{5,6} Since the mode of coordination of the hydrazido(1-) ligand in such a complex is of interest in order to gain information related to the stereochemical processes occurring during dinitrogen reduction, the structure of the above hydrazido(1-) complex, as the BF_4^- salt, was undertaken in order to confirm this highly unusual bonding mode.

EXPERIMENTAL

Deep red crystals of the title compound were kindly supplied by Professor Sutton of Simon Fraser University. Preliminary film data showed Laué symmetry 2/m, indicating a monoclinic system. The systematic absences ($h0\ell$, $\ell = 2n+1$ and $0k0$, $k = 2n+1$) uniquely defined the space group as $P2_1/c$. Accurate cell parameters were obtained by a least squares analysis of 12 accurately centered reflections, chosen from diverse regions of reciprocal space ($50^\circ \leq 2\theta \leq 75^\circ$, Cu K α X-radiation) and obtained using a narrow X-ray source. Table 1 contains the pertinent crystal data.

Data were collected by the θ - 2θ scan method on a Picker four-circle automated diffractometer, equipped with a scintillation counter and pulse height analyzer tuned to accept 90% of the Cu K α peak. Background counts were measured at

Table 1. Summary of Data and Intensity Collection for



Compound	$[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{NH}_2\text{NPh})][\text{BF}_4]$																																								
Formula Weight	507.98																																								
Formula	$\text{C}_{16}\text{H}_{17}\text{B}_1\text{F}_4\text{N}_2\text{W}_1$																																								
Cell Parameters																																									
a	8.5874 (6)																																								
b	10.4821 (8)																																								
c	19.5455 (14)																																								
β	107.176 (6)																																								
V	1680.9																																								
Z	4																																								
Density	2.007 g·cm ⁻³ (calcd.) 2.01(1) g·cm ⁻³ (exptl, floatation)																																								
Space Group	$\text{C}_{2h}^5 - \text{P}_{21}/c$																																								
Crystal Dimensions	0.231 x 0.158 x 0.180 mm																																								
Crystal volume	0.00359 mm ³																																								
Crystal Faces (and distances from an arbitrary origin within the crystal (mm))	<table><tr><td>1</td><td>0</td><td>0</td><td>0.069</td></tr><tr><td>1</td><td>0</td><td>-2</td><td>0.132</td></tr><tr><td>-2</td><td>-1</td><td>-6</td><td>0.080</td></tr><tr><td>-1</td><td>0</td><td>-1</td><td>0.060</td></tr><tr><td>-1</td><td>0</td><td>2</td><td>0.032</td></tr><tr><td>0</td><td>0</td><td>1</td><td>0.050</td></tr><tr><td>0</td><td>3</td><td>-1</td><td>0.125</td></tr><tr><td>0</td><td>1</td><td>1</td><td>0.093</td></tr><tr><td>0</td><td>-1</td><td>-1</td><td>0.110</td></tr><tr><td>0</td><td>-1</td><td>1</td><td>0.088</td></tr></table>	1	0	0	0.069	1	0	-2	0.132	-2	-1	-6	0.080	-1	0	-1	0.060	-1	0	2	0.032	0	0	1	0.050	0	3	-1	0.125	0	1	1	0.093	0	-1	-1	0.110	0	-1	1	0.088
1	0	0	0.069																																						
1	0	-2	0.132																																						
-2	-1	-6	0.080																																						
-1	0	-1	0.060																																						
-1	0	2	0.032																																						
0	0	1	0.050																																						
0	3	-1	0.125																																						
0	1	1	0.093																																						
0	-1	-1	0.110																																						
0	-1	1	0.088																																						
Temperature	20°C																																								
Radiation	Cu K α (λ = 1.540562 Å)																																								
μ	132.74 cm ⁻¹																																								
Range in Absorption																																									
Correction Factors	0.171 - 0.329																																								

Table 1, Continued

Receiving Aperture	3.4 mm wide x 5.2 mm high, 30 cm from the crystal
Takeoff Angle	3.0°
Scan Speed	2° in 2θ/min
Scan Range	0.80° below Kα ₁ to 0.80° above Kα ₂
Background Counting Time	2θ ≤ 99.00°, 20s; 2θ > 99.00°, 40s
2θ Limits	3.0° - 120.0°
2θ Limits for Centered Reflections	50.0° - 70.0°

Refinement Information

Unique Data Collected	2789
Unique Data Used	1972
<u>Model 1</u>	(Cp Rings Treated as Hindered Rotors)
Final Number of Parameters Varied	149
Error in Observation of Unit Weight	1.736 electrons
R	0.048
R _w	0.064
<u>Model 2</u>	(Cp Rings Treated as Individual Anisotropic Atoms)
Final number of Parameters Varied	225
Error in Observation of Unit Weight	1.640 electrons
R	0.045
R _w	0.057

both ends of the scan range with both crystal and counter stationary. The intensity of the peak (I), assuming approximate linearity of background, is given by

$$I = PK - (B_1 + B_2)t_P/t_B \quad (1)$$

where PK = peak count, t_P = peak scan time, t_B = the sum of the two background collection times and B_1 and B_2 are the background counts. Standard deviations in the intensities were calculated from equation (2):

$$\sigma(I) = (PK + t^2_{BT} + p^2 I^2)^{1/2} \quad (2)$$

where $BT = B_1 + B_2$, $t = t_P/t_B$ and p is an ignorance factor, which takes into account machine uncertainty and prevents an unreasonably high weighting being applied to reflections of high intensity.⁸ A value of 0.05 was used for p . The intensities of three standard reflections were measured every 100 reflections and were found to decrease by approximately 4% over the duration of the data collection. The observed intensities were corrected for this apparent decomposition.

The intensities of 2789 unique reflections ($3^\circ \leq 2\theta \leq 120^\circ$) were measured using Cu K α X-radiation. A total of 1972 reflections had $F_O^2 \geq 3\sigma(F_O^2)$ and were used in subsequent calculations. The data were reduced to structure factor amplitudes and standard deviations in the structure factors ($\sigma(F)$) by correction for Lorentz, polarization and absorp-

tion effects.⁹⁻¹² Similar procedures for data collection and reduction were followed on all subsequent structures.

STRUCTURE SOLUTION AND REFINEMENT

A Patterson map^{13,14} was computed between the limits $0.0 \leq u \leq 1.0$, $0.0 \leq v \leq 0.5$, $0.0 \leq w \leq 0.5$. The W-W vectors for the general position solution of the space group P_{21}/c are derived in Table 2. The origin peak in the Patterson map corresponds to the sum of the vectors between every atom and itself in the unit cell, and is roughly proportional to $\sum_i Z_i^2$, summed over the contents of the unit cell (*i.e.* $4 \times 74^2 + 16 \times 9^2 + 4 \times 5^2 + 8 \times 7^2 + 64 \times 6^2 + 68 \times 1^2 = 26064$). This peak is normalized to 1000 in the Fourier program used to calculate the vector map. Assuming comparable thermal parameters for all atoms, one expects the doubly weighted W-W vectors (see Table 2) to have an approximate, normalized value of 420 (*i.e.* $2 \times 74^2 / 26064 \times 1000$), and the singly weighted W-W vectors to have a value of 210. The top three peaks after the origin peak in the Patterson map correspond to the W-W vectors, and are listed with their assignments in Table 3. The weights of the next vectors start at 74, and correspond to W-C and W-N vectors. The W-W vectors are considerably stronger than the other vectors in the Patterson map, since the tungsten atom is so heavy compared to the other atoms in the unit cell. As a consequence, the Patterson map is quite useful in solving this structure,

Table 2. Derivation of the W-W Vectors for the Space Group P_{2_1}/c .

	x, y, z	$\bar{x}, \bar{y}, \bar{z}$	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	$x, \frac{1}{2}-y, \frac{1}{2}+z$
x, y, z	$0, 0, 0$	$2x, 2y, 2z$	$2x, \frac{1}{2}, \frac{1}{2}+2z$	$0, \frac{1}{2}+2y, \frac{1}{2}$
$\bar{x}, \bar{y}, \bar{z}$	$2\bar{x}, 2\bar{y}, 2\bar{z}$	$0, 0, 0$	$0, \frac{1}{2}-2y, \frac{1}{2}$	$2\bar{x}, \frac{1}{2}, \frac{1}{2}-2z$
$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	$2\bar{x}, \frac{1}{2}, \frac{1}{2}-2z$	$0, \frac{1}{2}+2y, \frac{1}{2}$	$0, 0, 0$	$2\bar{x}, 2y, 2\bar{z}$
$x, \frac{1}{2}-y, \frac{1}{2}+z$	$0, \frac{1}{2}-2y, \frac{1}{2}$	$2x, \frac{1}{2}, \frac{1}{2}+2z$	$2x, 2\bar{y}, 2z$	$0, 0, 0$

Vectors	Weights
$0, 0, 0$	4
$2x, \frac{1}{2}, \frac{1}{2}+2z$	2
$2\bar{x}, \frac{1}{2}, \frac{1}{2}-2z$	2
$0, \frac{1}{2}+2y, \frac{1}{2}$	2
$0, \frac{1}{2}-2y, \frac{1}{2}$	2
$2x, 2y, 2z$	1
$2\bar{x}, 2\bar{y}, 2\bar{z}$	1
$2x, 2\bar{y}, 2z$	1
$2\bar{x}, 2y, 2\bar{z}$	1

Table 3. Assignment of the Most Intense Patterson Map Vectors.

No.	u	v	w	Relative Weight	Assignment
1	0.000	0.037	0.500	408	$0, \frac{1}{2}+2y, \frac{1}{2}$
2	0.092	0.518	0.260	356	$2x, \frac{1}{2}, \frac{1}{2}+2z$
3	0.920	0.444	0.240	216	$2\bar{x}, 2\bar{y}, 2\bar{z}$

since the W-W vectors are unambiguous. Based on the vector assignment, the W position (0.05,0.27,0.38) was obtained and input into a full-matrix, least-squares refinement, which converged in 3 cycles to $R=0.219$ and $R_w=0.257$. The R values are defined as

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \quad (3)$$

and

$$R_w = \{ \Sigma w (|F_o| - |F_c|)^2 / \Sigma w |F_o|^2 \}^{1/2} \quad (4)$$

where $|F_o|$ and $|F_c|$ are the absolute values of the observed and calculated structure factors, respectively, and w , the weighting factor, is defined as $w = 1/\sigma^2(F)$. In the least squares refinement the function $\Sigma w (|F_o| - |F_c|)^2$ is minimized. Structure factors were calculated using the atomic scattering factors taken from Cromer and Waber's tabulation¹⁵ for all atoms except hydrogen, for which the values of Stewart *et al.*¹⁶ were used. Anomalous dispersion terms^{17,18} for W were included in F_c .

An electron density difference map, phased on the W position yielded the position of all non-hydrogen atoms in the cation. The BF_4^- anion was found after the next least-squares refinement and electron density difference map. The data were corrected for absorption effects by Gaussian integration.

The cyclopentadienyl carbons were refined by two different techniques. In the first method, the carbon atoms

of these rings were treated as hindered rotor groups¹⁹ with D_{5h} symmetry. The positions, orientations, and the radii of these groups and their barriers to libration perpendicular to their group planes were refined. This refinement method has the important advantage over individual atom treatments that more chemically reasonable C-C distances for the Cp rings are obtained. Furthermore, significantly fewer parameters are refined using this technique (see Table 1). In the second method the cyclopentadienyl carbon atoms were refined as individual anisotropic atoms, where the form of the thermal ellipsoid used was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The converged refinements for both models are briefly compared (*vide infra*), however, in spite of the advantages of the rigid body refinement only the individual atom refinement is reported in detail owing to the better standard deviations in the parameters of interest obtained by using this model. In both refinement techniques, the phenyl and cyclopentadienyl hydrogen atoms were included as fixed contributions in the final few least squares refinements. The idealized positions of the phenyl hydrogen atoms were calculated from the geometries about the attached carbon atom using a C-H distance of 0.95 Å. These hydrogen atoms were given isotropic thermal parameters of 1 Å² greater than the equivalent isotropic B of their attached carbon atoms. The cyclopentadienyl hydrogen atoms were included as hindered

rotor groups in both refinement methods using the group parameters obtained from the previous hindered rotor refinement of the Cp carbon atoms. The group thermal parameters were set at 1 \AA^2 greater than those of the corresponding carbon atom group. The remaining non-hydrogen atoms were refined individually with anisotropic thermal parameters, while the two hydrogen atoms on N(1) were refined individually with isotropic thermal parameters. The final model, with individual anisotropic Cp carbon atoms, converged at $R = 0.045$ and $R_w = 0.057$ for 225 variables. In the final electron density difference map, the highest 20 residuals (0.03 to 0.90 e/\AA^3) were in the vicinities of the W atom and the BF_4^- anion. A typical carbon atom on earlier Fourier maps had an intensity of approximately 4.00 e/\AA^3 . Some difficulty was encountered in refining the BF_4^- anion owing to disorder of this group. More sophisticated models describing this disorder were not used, however, since the four fluorine positions used were clearly the most obvious from difference Fourier calculations (peaks from $2.5 - 5.4 \text{ e/\AA}^3$). In addition, the added effort was not judged worthwhile as no change in the parameters of interest was anticipated; certainly there was no significant change in these parameters between the refinements before and after inclusion of the anion.

The programs used in the solution and refinement of the structure, and presentation of data are listed briefly in Appendix I.

RESULTS

A stereoview of the unit cell is shown in Figure 3. The crystallographic a axis is going into the page, the b axis is from left to right, and the c axis is from top to bottom. In this and all subsequent diagrams unless otherwise noted, vibrational ellipsoids of 20% are shown for all atoms, except hydrogens which are shown artificially small. Figure 4 shows a perspective view of the cation, including the numbering scheme used (phenyl hydrogen atoms have the same number as their attached carbon atom) and some relevant bond lengths. The representation of the cation shown in Figure 5 and viewed in the W-N(1)-N(2) plane, shows the orientation of the phenyl ring in relation to the W-N(1)-N(2) plane and the Cp planes. The final positional and thermal parameters for the non-group atoms are given in Table 4. The idealized positional and thermal parameters for the hydrogen atoms are given in Table 5. Selected interatomic distances and angles are listed in Tables 6 and 7, respectively, while least squares plane calculations are in Table 8. A listing of the observed and calculated structure factor amplitudes is available.²⁰

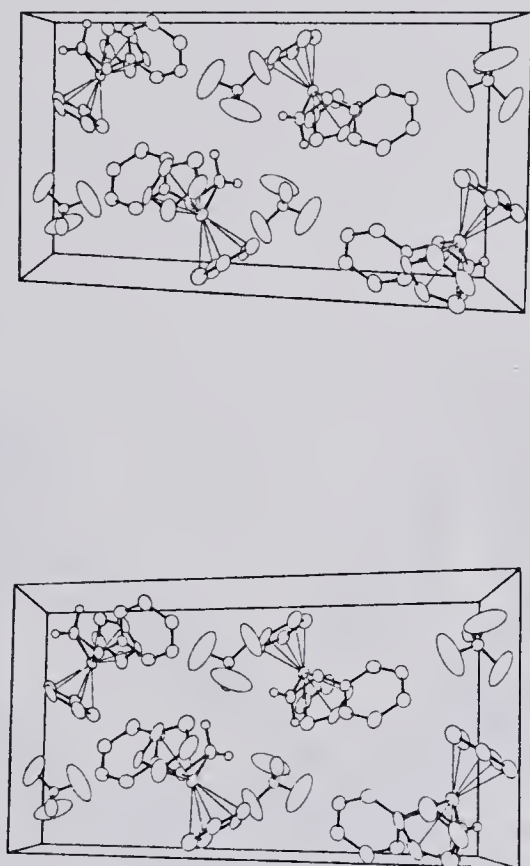


Figure 3. Cell Packing Diagram of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{H}_2\text{NNPh})][\text{BF}_4]$.

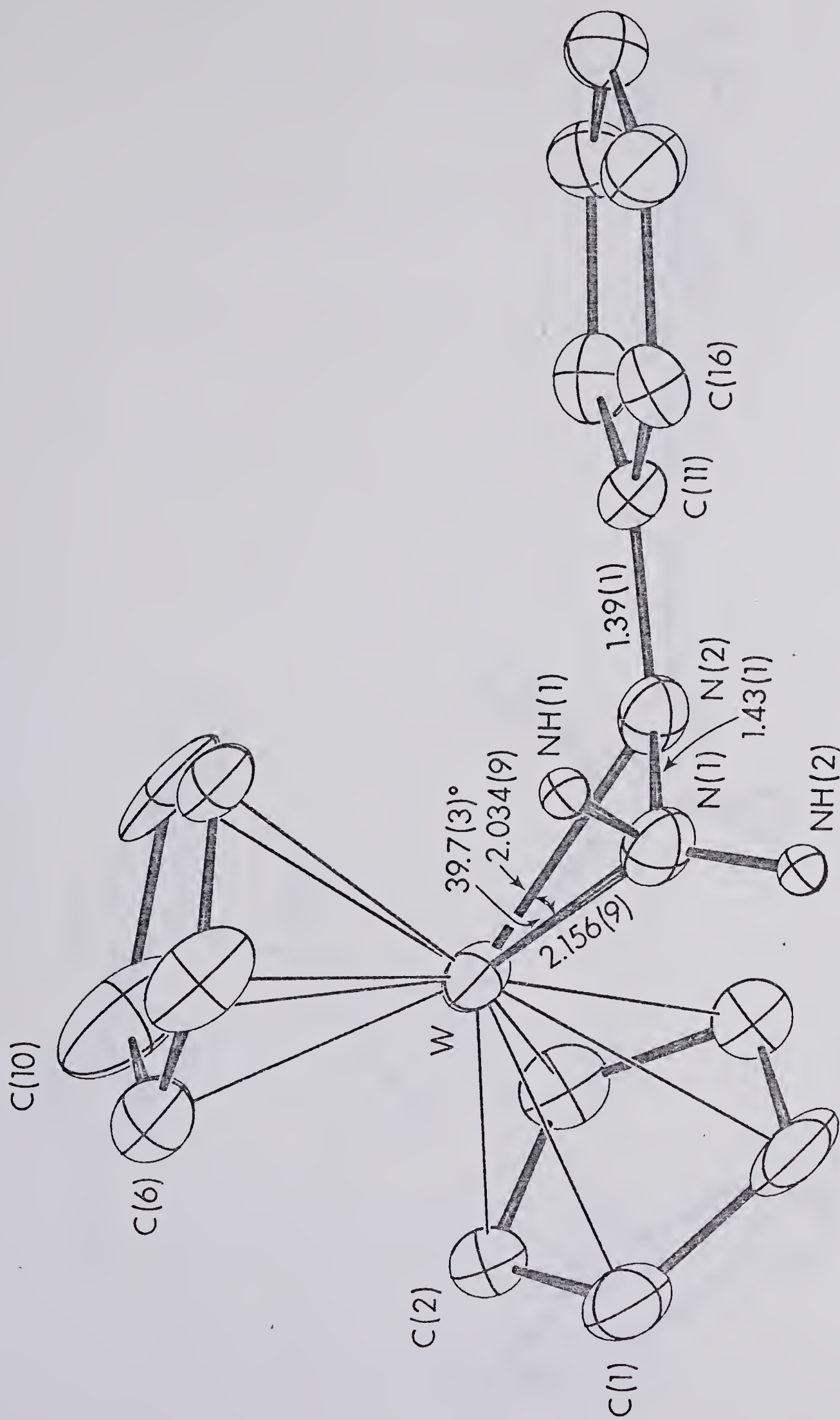


Figure 4. Perspective View of the $[(\eta^5\text{-C}_6\text{H}_5)_2\text{W}(\text{H}_2\text{NNPh})]^+$ Cation.

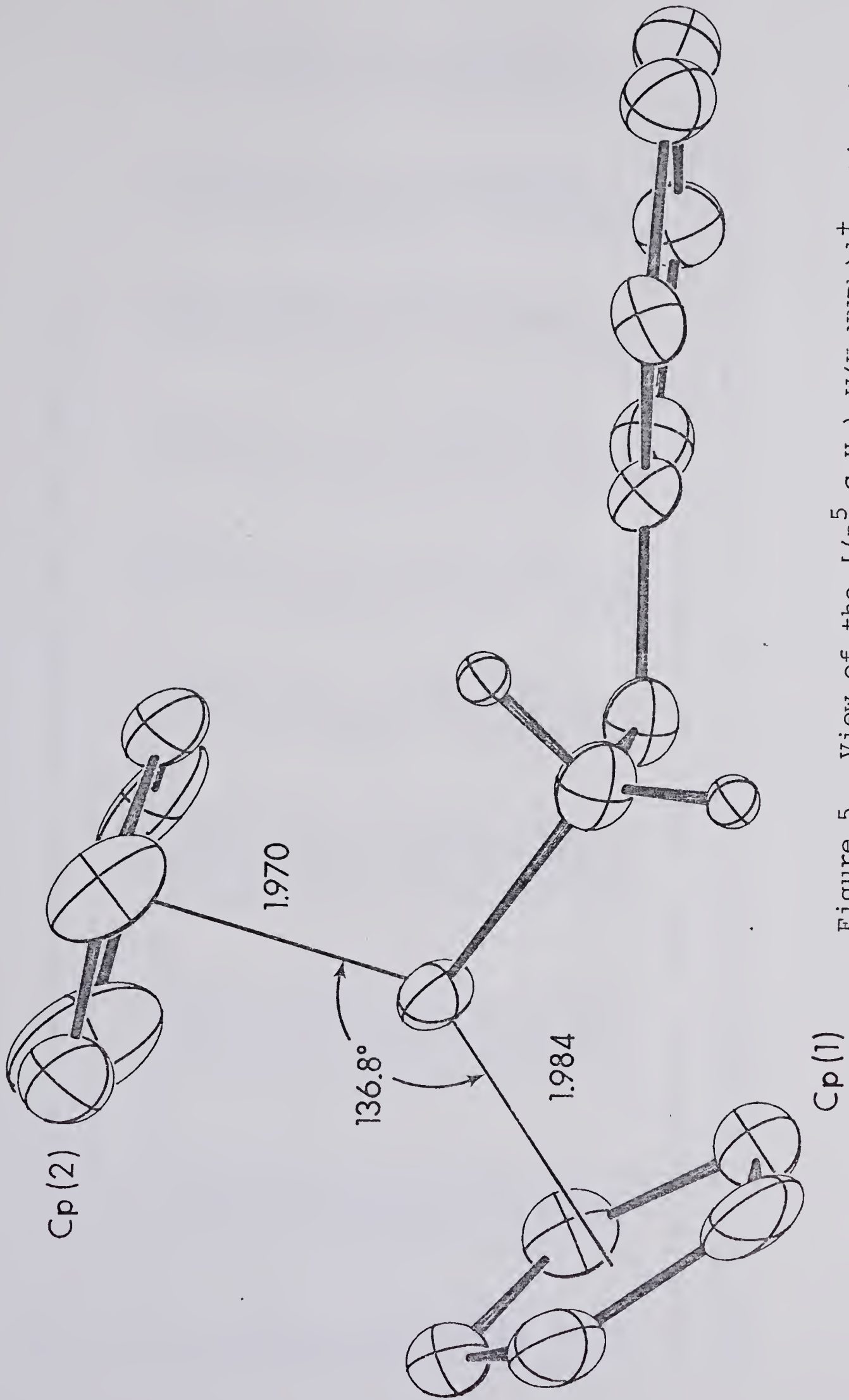


Figure 5. View of the $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{H}_2\text{NNPh})]^+$ cation in the Plane of W-N(1)-N(2) .

Table 4. Positional and Thermal Parameters For the Non-Hydrogen Atoms of [Cp2W(NH2NPh)][BF4].

Atom	a				b							
	x	y	z	U11	U22	U33	U12	U13	U23			
W	0.04371(6)	0.27560(5)	0.38366(2)	6.00(3)	6.14(3)	6.00(3)	0.50(2)	0.57(2)	0.95(2)			
N(1)	0.266(1)	0.385(1)	0.4153(5)	7.2(6)	7.8(7)	6.3(5)	0.2(5)	0.3(4)	-0.4(5)			
N(2)	0.252(1)	0.3023(8)	0.3557(4)	7.7(5)	6.8(6)	5.9(5)	0.2(4)	0.7(4)	-0.4(4)			
C(1)	0.044(2)	0.171(1)	0.4859(6)	11(1)	9.4(9)	7.3(7)	-0.7(8)	2.4(7)	1.9(7)			
C(2)	-0.082(2)	0.118(1)	0.4293(7)	9.4(8)	7.0(8)	10.0(9)	-0.2(7)	3.1(7)	2.0(7)			
C(3)	-0.014(2)	0.058(2)	0.3810(8)	11(1)	9(1)	10(1)	0.6(8)	3.4(9)	1.3(8)			
C(4)	0.154(2)	0.069(1)	0.407(1)	10(1)	8(1)	15(1)	3.1(8)	5(1)	4.0(9)			
C(5)	0.192(2)	0.138(2)	0.4728(8)	7.9(8)	10(1)	11(1)	0.7(7)	0.6(8)	5.9(9)			
C(6)	-0.187(2)	0.390(3)	0.379(1)	10(1)	15(2)	15(2)	6(1)	6(1)	7(1)			
C(7)	-0.079(2)	0.476(2)	0.372(1)	11(1)	7(1)	15(2)	4.0(9)	0(1)	-0.9(9)			
C(8)	-0.039(2)	0.446(2)	0.311(1)	10(1)	9(1)	12(1)	3.3(9)	2(1)	4.7(9)			
C(9)	-0.123(3)	0.348(2)	0.2774(7)	13(1)	17(2)	6.9(8)	7(1)	-2.7(9)	-0(1)			
C(10)	-0.225(2)	0.308(2)	0.323(2)	5.7(8)	11(2)	25(3)	-0.7(8)	-4(1)	4(2)			
C(11)	0.302(1)	0.345(1)	0.2982(5)	5.3(5)	6.1(7)	5.7(5)	1.1(4)	1.0(4)	0.3(5)			
C(12)	0.260(2)	0.270(1)	0.2373(7)	8.4(8)	7.0(7)	8.9(8)	0.1(6)	1.5(6)	-0.0(6)			
C(13)	0.318(2)	0.298(1)	0.1805(7)	12(1)	8(1)	7.8(8)	0.6(7)	3.8(7)	-0.8(6)			
C(14)	0.405(2)	0.407(2)	0.1802(7)	8.0(8)	12(1)	7.9(8)	0.8(8)	2.8(6)	0.3(8)			
C(15)	0.446(1)	0.483(1)	0.2413(7)	5.6(5)	8.2(9)	12(1)	0.3(5)	1.8(6)	1.9(8)			
C(16)	0.394(1)	0.454(1)	0.2994(6)	5.8(6)	7.6(8)	8.6(7)	0.2(5)	2.0(5)	-0.9(6)			
B	-0.348(2)	0.225(1)	0.0503(7)	6.4(7)	6.4(7)	7.0(7)	1.8(6)	0.0(6)	-0.5(6)			
F(1)	-0.486(1)	0.163(1)	0.0555(5)	10.6(6)	18.0(9)	12.2(7)	-3.5(6)	-0.4(5)	4.6(7)			
F(2)	-0.250(3)	0.152(2)	0.043(2)	36(3)	19(2)	62(4)	15(2)	36(3)	17(2)			
F(3)	-0.290(4)	0.264(3)	0.106(1)	44(4)	66(5)	20(2)	-39(4)	14(2)	-17(2)			
F(4)	-0.375(2)	0.310(2)	0.004(1)	18(1)	26(2)	34(2)	1(1)	4(1)	19(2)			

a Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

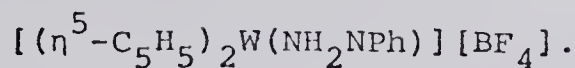
b The form of the thermal ellipsoid is: $\exp[-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^2$.

Table 5. Idealized Positional and Thermal Parameters For the Hydrogen Atoms of [Cp2W(NH2NPh)](BF4).

Atom	x	y	z	B(A ²)	Atom	x	y	z	B(A ²)
NH(1) ^a	0.25(1)	0.49(1)	0.404(5)	7(3)	H(3)	-0.0746	0.0157	0.3358	6.54
NH(2) ^a	0.37(2)	0.37(1)	0.452(6)	8(3)	H(4)	0.2330	0.0355	0.3847	8.30
H(12)	0.2022	0.1906	0.2370	7.33	H(5)	0.2983	0.1585	0.5016	7.33
H(13)	0.2924	0.2426	0.1385	8.71	H(6)	-0.2415	0.3825	0.4179	8.71
H(14)	0.4465	0.4277	0.1407	8.19	H(7)	-0.0317	0.5436	0.4052	8.19
H(15)	0.5104	0.5608	0.2414	7.94	H(8)	0.0380	0.4937	0.2908	7.94
H(16)	0.4202	0.5089	0.3399	7.28	H(9)	-0.1286	0.3018	0.2328	7.28
H(1)	0.0310	0.2147	0.5250	7.28	H(10)	-0.3014	0.2331	0.3113	7.28
H(2)	-0.1995	0.1265	0.4225	7.28					

^a Refined as an isotropic atom.

Table 6. Selected Interatomic Distances (Å) in



BONDED CONTACTS

W-N(1)	2.156(9)	C(3)-C(4)	1.38(2)
W-N(2)	2.034(9)	C(4)-C(5)	1.43(2)
W-C(1)	2.28(1)	C(5)-C(1)	1.41(2)
W-C(2)	2.29(1)	C(6)-C(7)	1.34(2)
W-C(3)	2.33(2)	C(7)-C(8)	1.36(2)
W-C(4)	2.36(1)	C(8)-C(9)	1.32(2)
W-C(5)	2.33(1)	C(9)-C(10)	1.49(3)
W-C(6)	2.29(1)	C(10)-C(6)	1.35(3)
W-C(7)	2.34(1)	C(11)-C(12)	1.38(2)
W-C(8)	2.26(1)	C(12)-C(13)	1.37(2)
W-C(9)	2.28(1)	C(13)-C(14)	1.37(2)
W-C(10)	2.29(1)	C(14)-C(15)	1.39(2)
N(1)-N(2)	1.43(1)	C(15)-C(16)	1.37(2)
N(1)-NH(1)	1.08(11)	C(16)-C(11)	1.39(1)
N(1)-NH(2)	0.97(13)	B-F(1)	1.38(2)
N(2)-C(11)	1.39(1)	B-F(2)	1.18(2)
C(1)-C(2)	1.41(2)	B-F(3)	1.14(2)
C(2)-C(3)	1.40(2)	B-F(4)	1.24(2)

NON-BONDED CONTACTS

F(1)-NH(2)	2.1(1) ^a	H(2)-C(6)	2.90
F(2)-NH(1)	2.0(1) ^b	H(8)-C(11)	2.72
F(3)-H(9)	2.48	H(10)-C(2)	2.78
NH(1)-H(16)	2.19	H(12)-N(2)	2.52
NH(1)-H(8)	2.43	H(16)-N(1)	2.60
H(2)-H(10)	2.37	H(16)-N(2)	2.67
H(2)-C(10)	2.68		

HINDERED ROTOR PARAMETERS

	Cp(1)		Cp(2)
C-C	1.421(6)	C-C	1.423(6)
Bd = 1.82 ^c		Bd = 0.42	

^a NH(2) is associated with the molecule at the general equivalent position $x, \frac{1}{2}-y, \frac{1}{2}+z$.

^b NH(1) is associated with the molecule at the general equivalent position $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$.

^c Bd is the barrier to libration in units of $2kT$, where k is the Boltzmann constant and T is the temperature.

Table 7. Selected Angles (deg) in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{H}_2\text{NNPh})][\text{BF}_4]$

Bond Angles

N(1)-W-N(2)	39.7(3)	C(1)-C(2)-C(3)	109(1)
W-N(1)-NH(1)	115(6)	C(2)-C(3)-C(4)	108(1)
W-N(1)-NH(2)	133(8)	C(3)-C(4)-C(5)	108(1)
W-N(1)-N(2)	65.6(5)	C(4)-C(5)-C(1)	108(1)
W-N(2)-N(1)	74.8(6)	C(5)-C(1)-C(2)	106(1)
W-N(2)-C(11)	140.1(6)	C(6)-C(7)-C(8)	108(2)
N(2)-N(1)-NH(1)	117(5)	C(7)-C(8)-C(9)	112(2)
N(2)-N(1)-NH(2)	112(7)	C(8)-C(9)-C(10)	105(2)
NH(1)-N(1)-NH(2)	107(10)	C(9)-C(10)-C(6)	105(2)
N(1)-N(2)-C(11)	119.4(9)	C(10)-C(6)-C(7)	111(2)
N(2)-C(11)-C(12)	117(1)	F(1)-B-F(2)	111(2)
N(2)-C(11)-C(16)	124.2(9)	F(1)-B-F(3)	104(2)
C(11)-C(12)-C(13)	121(1)	F(1)-B-F(4)	114(1)
C(12)-C(13)-C(14)	120(1)	F(2)-B-F(3)	103(2)
C(13)-C(14)-C(15)	118(1)	F(2)-B-F(4)	112(2)
C(14)-C(15)-C(16)	121(1)	F(3)-B-F(4)	112(2)
C(15)-C(16)-C(11)	119(1)	N(1)-NH(1)-F(2)	139(8) ^a
C(16)-C(11)-C(12)	119(1)	N(1)-NH(2)-F(1)	154(10) ^b
CR1-W-CR2	136.8		

Torsion Angles

NH(1)-N(1)-N(2)-C(11)	32.3	C(3)-CR1-CR2-C(9)	33.5
C(1)-CR1-CR2-C(6)	31.2	C(4)-CR1-CR2-C(8)	34.7
C(2)-CR1-CR2-C(10)	32.1	C(5)-CR1-CR2-C(7)	33.2

Vector-Plane Normal Angles

N(2)-N(1)	NH(1)-N(1)-NH(2)	44(7) ^c
N(2)-C(11)	W-N(1)-N(2)	55.5(8) ^c

^aF(2) is associated with the molecule at the general equivalent position \bar{x} , $\frac{1}{2}+y$, $\frac{1}{2}-z$.

^bF(1) is associated with the molecule at the general equivalent position x , $\frac{1}{2}-y$, $\frac{1}{2}+z$.

^cAngle between the vector defined by the first two atoms and the normal to the plane defined by the last three atoms.

Table 8. Least-Squares Plane Calculations^a

plane no.	equation
1	$-0.2728X + 0.7327Y - 0.6235Z + 1.8482 = 0$
2	$0.1126X + 0.8539Y - 0.5081Z + 3.3639 = 0$
3	$-0.6073X + 0.6045Y - 0.5155Z - 1.1396 = 0$
4	$0.1702X - 0.4923Y - 0.8536Z + 7.8509 = 0$
5	$-0.7532X + 0.5300Y - 0.3897Z + 0.9023 = 0$
6	$-0.8250X + 0.3563Y - 0.4387Z + 1.8727 = 0$

Deviations from the Planes (Å)
Plane no.

Atom	1	2	3	4	5	6
W	0.0	1.9839 (5) ^b	-1.9695 (5) ^b	0.0		
N(1)	0.0			-0.774 (9) ^b		0.0
N(2)	0.0			0.639 (8) ^b		0.0
C(1)		0.01 (1)				
C(2)		-0.01 (1)				
C(3)		0.01 (2)				
C(4)		0.00 (2)				
C(5)		0.01 (2)				
C(6)			-0.02 (2)			
C(7)			0.02 (2)			
C(8)			-0.01 (2)			
C(9)			0.01 (2)			
C(10)			0.00 (2)			
C(11)	0.79 (1) ^b				-0.01 (1)	0.0
C(12)					0.03 (1)	
C(13)					-0.03 (2)	
C(14)					0.02 (1)	
C(15)					-0.01 (1)	
C(16)					0.00 (1)	
CR1				0.0		
CR2				0.0		

Dihedral Angles Between Planes

Plane A	Plane B	angle (deg)
1	2	24.3
1	3	21.6
1	4	82.8
1	5	33.2
1	6	40.6
2	3	44.8
5	6	11.9

^aX, Y and Z are the orthogonal coordinates (Å) with X along the a axis, Y in the (a-b) plane and Z along the c* axis.

^bNot included in the least squares plane calculation.

DESCRIPTION OF STRUCTURE

The structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{NH}_2\text{NPh})][\text{BF}_4]$ consists of four monomeric anions and cations per unit cell, as shown in Figure 3. The description of the tetrafluoroborate anion is somewhat inadequate owing to the disorder of this group. As a result, the thermal parameters for the four fluorine atoms are large (Table 4) and much of the unassigned electron density in the final difference Fourier map lies in the region around the anion. In spite of the disorder, however, the anion clearly shows the expected tetrahedral configuration about the boron atom. The B-F distances, which range from 1.14(2) to 1.38(2) Å (Table 6) are somewhat shorter than other reported values,²¹ but are not unreasonable considering the disorder. In addition the F-B-F angles, ranging from 103(2)° to 114(1)° (Table 7) are as expected. There are two significant non-bonded contacts between the fluorine atoms and the hydrogen atoms of the hydrazido ligand (F(1)-NH(2), 2.1(1) Å; F(2)-NH(1), 2.0(1) Å), both of which are much less than the sum of their van der Waals radii (2.57 Å).²² The corresponding N(1)-NH(1)-F(2) and N(1)-NH(2)-F(1) angles are 139(8)° and 154(10)°, respectively.

The $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{NH}_2\text{NPh})]^+$ cation can be viewed as having pseudotetrahedral coordination about the tungsten atom, with the $(\eta^5\text{-C}_5\text{H}_5)$ rings each occupying one coordination site and the two nitrogen atoms of the "side-on"

bonded phenylhydrazido(1-) ligand occupying the other sites. However, the coordination angles are significantly distorted from the ideal geometry owing to the large bulk of the Cp rings and the small bite angle of the hydrazido ligand; the CR1-W-CR2 angle is 136.8° while the N(1)-W-N(2) angle is $39.7(3)^\circ$. There are no unusually short non-bonded interactions between the two cyclopentadienyl rings. The metal-carbon bond lengths are in the range 2.28(1) to 2.36(1) Å for Ring 1 (average, 2.32(3) Å) and 2.26(1) to 2.34(1) for Ring 2 (average, 2.29(3) Å). These M-C distances are quite typical for CpML_n compounds,^{23,24} and agree well with the values found for the monoinserted product, $[\text{Cp}_2\text{WH}(\text{NNHC}_6\text{H}_4\text{F})][\text{PF}_6]$.⁷ The perpendicular distances between the metal and the ring planes are 1.9839(5) Å (Ring 1) and 1.9695(5) Å (Ring 2). They agree well with the metal-ring center distances (Ring 1, 1.985 Å and Ring 2, 1.971) indicating that each ring is well centered above the metal atom.

A comparison of Cp-M-Cp angles within a series of Cp_2ML_2 complexes containing staggered Cp groups indicates that the CR1-W-CR2 angle (136.8°) in the present compound, although comparable to other values (126.0 to 135.3°), is somewhat larger. An analysis of these angles²³ indicates that the larger angles tend to correspond to shorter Cp-M distances, implying that these angles are governed primarily by intramolecular repulsions. The small N(1)-W-N(2) angle ($39.7(3)^\circ$) in the present compound probably results in a less crowded

environment for the Cp rings and consequently in a larger CR1-W-CR2 angle. In $[\text{Cp}_2\text{Ti}(\eta^2\text{-C}_6\text{H}_5\text{CN-2,6-(CH}_3)_2\text{C}_6\text{H}_3)]$,²⁵ which also has a small ligand bite angle ($35.1(2)^\circ$), the Cp-Ti-Cp angle is again larger than that expected from the Cp-Ti distances.

The cyclopentadienyl rings assume a staggered conformation with C-CR1-CR2-C torsion angles averaging 32.9° (see Table 7). Other studies on similar systems have indicated that these ring conformations are governed primarily by crystal packing.²³ The carbon atoms in each of the rings are coplanar to within 0.01 \AA (Ring 1) and 0.02 \AA (Ring 2). Within each ring the C-C bond distances are in the range $1.38(2)$ to $1.43(2) \text{ \AA}$ for Ring 1, (average, $1.41(3) \text{ \AA}$) and $1.32(2)$ to $1.49(2) \text{ \AA}$ for Ring 2, (average, $1.37(6) \text{ \AA}$). These average values are shorter than the predicted value of 1.43 \AA .²⁶ However, this apparent shortening is a consequence of thermal libration of the rings and is a general feature of $\eta^5\text{-C}_5\text{H}_5$ compounds where the Cp rings are refined as individual atoms. In this respect the hindered rotor refinement is useful since the ring radii are allowed to vary as the ring librates about the metal-CR axis. This model for the Cp groups minimizes the ring contraction that is so common when individual atom refinements are used.²³ From the hindered rotor refinement the C-C distances ($1.421(6)$ and $1.423(6) \text{ \AA}$ for rings 1 and 2, respectively) agree very well with each other and with the predicted value. In the individual atom refinement of the Cp rings the group with the shorter

average C-C distance (Ring 2) also has the higher thermal parameters and corresponds to the group having the lower barrier to libration in the hindered rotor description (Table 6).

The phenylhydrazido ligand is side-on bonded to the W atom through the two nitrogen atoms. The W-N(1)-N(2) plane essentially bisects the CR1-W-CR2 angle and the dihedral angle between these planes is 82.8° (Table 8). The two metal-nitrogen bonds are noticeably different, with W-N(1), involving the four-coordinate nitrogen atom ($2.156(9) \text{ \AA}$), being significantly longer than W-N(2) ($2.034(9) \text{ \AA}$), which involves the three-coordinate nitrogen atom. The shorter distance may result from donation of the available lone pair on N(2) to the metal, although the W atom formally has an 18-electron configuration already. Similar electron donation from the chloro ligands to the metal atoms is believed responsible for the short M-Cl bonds in Cp_2MCl_2 complexes.²³ The possible involvement of the free lone pair on N(2) may also explain the phenyl group orientation (see Figure 5) and the solution NMR characteristics^{5,6} (*vide infra*). The W-N bonds can be compared to typical W-N single bonds in pyridine complexes which lie in the range 2.23 to 2.32 \AA .^{27,28} On the other hand, hydrazido (2-) complexes, with M-N bond orders greater than one, typically have M-N bond lengths of *ca.* 1.75 \AA .²⁹ While there are no other reported dihapto

hydrazido(1-) metal compounds, a comparison can be made with the following related compounds: $\{(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}\}_2(\mu\text{N-NMe}_2)^{30}$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}(\text{NH}_2\text{NHPH})][\text{BF}_4]^{31}$. In these species the Mo-N bonds involving the four-coordinate nitrogen atoms (2.133(12) to 2.184(3) Å) are again significantly longer than that of the three-coordinate nitrogen atom (2.058(12) Å), and both classes of W-N bonds compare well with the analogous distances in the present hydrazido(1-) complex. As a consequence of the above asymmetric bonding of the hydrazido(1-) ligand, the two nitrogen atoms are not equally spaced from the CR1-W-CR2 plane; instead N(1) is 0.774(9) Å from the plane, and N(2) is displaced 0.639(8) Å from this plane.

The N-N bond length in the title complex (1.43(1) Å) compares well with the values for the two molybdenum hydrazido compounds (1.400(17) Å³⁰ and 1.430(5) Å³¹) and is typical of an N-N single bond. By comparison, a characteristic N-N double bond is *ca.* 1.23 Å.³² Both hydrogen atoms on N(1) were located and refined, resulting in normal N-H bond distances of 1.08(11) Å for N(1)-NH(1) and 0.97(13) Å for N(1)-NH(2). The NH(1)-N(1)-NH(2) angle is 107(10)° close to that expected for a tetrahedral coordination about the nitrogen, and the angle of the N(2)-N(1) vector to the normal of the NH(1)-N(1)-NH(2) plane is 44(7)°, comparable to the calculated value of *ca.* 35.3° for an idealized tetrahedral coordination. No electron density that would be consistent

with a hydrogen atom is observed in the vicinity of N(2). This is consistent with the solution NMR studies⁶ which show both protons on N(1) and none on N(2). It is somewhat surprising that both hydrazido hydrogen atoms are bonded to N(1) since in the initial monoinserted product the hydrogen atom and the phenyl ring are bonded to the same nitrogen atom,^{6,7} indicating that in the second insertion process the transfer of a hydrogen atom from W to N(1) is accompanied by a hydrogen transfer from N(2) to N(1). The N(2)-C(11) bond (1.39(1) Å) is somewhat shorter than a normal N-C single bond (1.43 Å) involving an sp^2 hybridized carbon atom,²² but is not particularly unusual. The C-C lengths in the phenyl ring are all reasonable and the carbon atoms of the ring are coplanar to within 0.03 Å (Table 8). The phenyl ring is bent out of the W-N(1)-N(2) plane by 34.5(8)° towards Cp ring 2 with C(11) being 0.79(1) Å out of this plane (see Figure 5).

Although the phenyl group orientation on N(2) is characteristic of sp^3 hybridization of this atom, some distortion is evident. Instead of an eclipsed configuration about the N(1)-N(2) bond, the phenyl group is staggered with respect to the N(1) hydrogen atoms (the NH(1)-N(1)-N(2)-C(11) torsion angle is 32.3°). This twist about the N(1)-N(2) bond may result because of involvement of the lone pair of electrons on N(2) in bonding with the metal atom, as the twist is in the proper direction for such an interaction

and the short W-N(2) bond is consistent with some multiple bond character (*vide supra*). It is also possible that this distortion from eclipsed conformations about N(1) and N(2) may be steric in origin, resulting from non-bonded interactions between the cyclopentadienyl ring 2 and the phenyl ring pushing the phenyl ring towards the W-N(1)-N(2) plane. The only such contact which is significant (C(11)-H(8) = 2.72 Å) would favour this distortion. However, we have already noted that the C1-W-C2 angle is greater than is generally observed, indicating that the cyclopentadienyl groups are not overly crowded. The staggered conformation may also result from steric interactions between NH(1) and H(16) since this contact (2.19 Å) is rather short.

DISCUSSION

There is a notable lack of structural information on Cp₂ML complexes, in which L is a side-on coordinated ligand, thereby limiting any comparison of structural parameters. Only the present structure and that of [Cp₂Ti(η²-C₆H₅CN-2,6-(CH₃)₂C₆H₃)]²⁵ are known to us. At the first glance the structural differences between these complexes and the related Cp₂ML₂ species seem to result primarily from the reduced steric demands of the η²-coordinated ligands as compared to the two sigma bonded ligands (*vide supra*). However, a more detailed analysis of the differences in the two types of systems must await further structural character-

izations of Cp_2ML complexes containing side-on coordinated ligands.

The structural determination of the present complex, besides providing some of this badly needed information has also proven useful in understanding the ^1H NMR data⁶ which indicate that the two cyclopentadienyl rings are equivalent, even at low temperature. This equivalence could result from the complete planarity of the hydrazido(1-) ligand framework in the plane bisecting the angle between the two Cp rings, or from a fluctuational process which averages the Cp ring environments. The solid state data indicate that the two cyclopentadienyl rings are inequivalent since the phenyl group is significantly displaced from the W-N(1)-N(2) plane towards Cp Ring 2. As suggested earlier, this phenyl ring orientation may result from involvement of the free lone pair on atom N(2) in bonding with the W atom. This proposed bonding would account for the short W-N(2) bond length and, if the Cp equivalence results from "flipping" of the phenyl ring from one side of the W-N(1)-N(2) plane to the other, could also explain the facility of this process. The involvement of the N(2) lone pair in bonding with the W atom would allow the "flipping" mechanism to proceed by a concerted process with the simultaneous involvement of two N(2) electron pairs with the W atom.

The $[(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{NH}_2\text{NPh})]^+$ cation is believed to be the first structurally characterized complex containing a hydra-

zido(1-) ligand,³³ an important intermediate species in model systems for the reduction of dinitrogen. Although Hidai and coworkers³⁴ have reported the structure of a species which they claim is a hydrazido(1-) complex, $[\text{WClBr}_2(\text{N}_2\text{H}_3)(\text{PMe}_2\text{Ph})_3]$, their crystallographic evidence does not support this claim, and even the authors admit doubt concerning its formulation. Certainly in solution their evidence for a species containing the NHNH_2 ligand is convincing, but their solid state structure is more characteristic of a hydrazido(2-) ligand with a $\text{W}=\text{N}=\text{NH}_2$ moiety. All of their structural parameters, including the short W-N bond ($1.80(4)$ Å), the almost linear W-N-N fragment ($177(5)^\circ$) and the N-N distance ($1.24(6)$ Å) which is characteristic of an $\text{N}=\text{N}$ double bond, support a terminally bonded hydrazido(2-) formulation. Furthermore, this structure bears a remarkable resemblance to the hydrazido(2-) complex, $[\text{W}(\text{quinolin-8-olate})(\text{NNH}_2)(\text{PMe}_2\text{Ph})_3]\text{I}$, recently reported by Chatt and coworkers.²⁹ The authors' suggestion³⁴ that the complex $[\text{WClBr}_2(\text{N}_2\text{H}_3)(\text{PMe}_2\text{Ph})_3]$ may actually contain a $\text{W}-\text{N}-\text{NH}_3^+$ moiety is also not consistent with the observed structural parameters, in particular the short N-N distance. Our formulation of the title complex as a hydrazido(1-) species, on the other hand, is quite unambiguous with all parameters being consistent with this formulation; even the hydrazido hydrogen atom positions are well defined.

The present structural determination is particularly relevant to our understanding of dinitrogen reduction. In-

sertion reactions of aryldiazo cations into metal-hydride bonds have long been considered as useful model systems for nitrogen fixation. The reaction of Cp_2WH_2 with $(\text{N}_2\text{Ar})^+$ produces not only the mono-inserted hydrazido(2-) product, $[\text{Cp}_2\text{WH}(\text{NNHAr})]^+$,⁷ but also the doubly-inserted hydrazido(1-) product, $[\text{Cp}_2\text{W}(\text{NH}_2\text{NAr})]^+$. The mechanism of the rearrangement from the mono-inserted complex, a monohydrido species with a doubly bent hydrazido ligand⁷ to that of the double insertion product, where both hydrogens are coordinated to the first nitrogen atom, and the ligand is side-on coordinated, is unknown, but of considerable interest. In addition, the latter species has the diazo moiety activated by the W atom, suggesting the possibility of further reduction of this ligand.

Double insertion reactions involving Cp_2MH_2 compounds ($\text{M} = \text{Mo}, \text{W}$) have been reported,³⁵ for example in the reactions of azobenzene and diazofluorene. However the double insertion products were not isolated, undergoing instead, loss of the reduced molecule and subsequent attack of the " Cp_2M " species by excess ligand. As such, the title complex represents the first characterized species resulting from the double insertion into both metal-hydride bonds of a dihydride complex. This compound is one step closer to a totally reduced N_2Ph^+ cation than the products obtained from the usual monoinsertion reactions and represents an important intermediate in model system studies for the reduction of dinitrogen.

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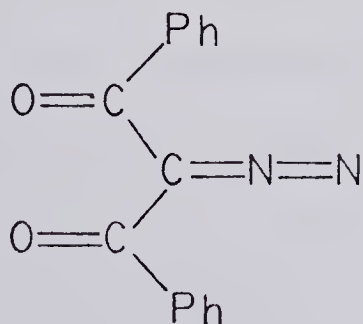
Chapter III.

The Structure of Dibenzoyldiazomethane.

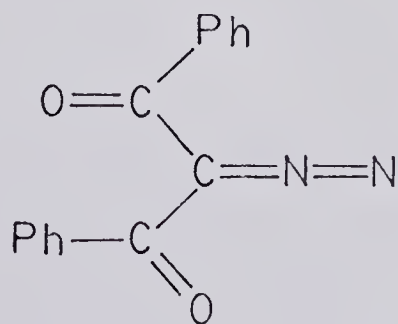
INTRODUCTION

Diazoalkane molecules have been studied for many years and their chemistry is well documented.¹ Although synthetically, they are extremely useful reagents,² very few structural studies have been done on free diazoalkane molecules, owing to the limited stability of most diazo groups. Dibenzoyldiazomethane, $(C_6H_5COCN_2COC_6H_5)$, is unusual in this regard, in that the molecule may be isolated as a relatively stable, crystalline product.

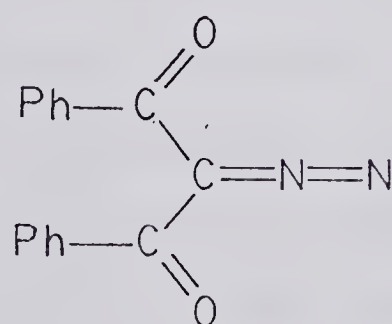
In dibenzoyldiazomethane, a planar conformation will be favored owing to the possibility of π -delocalization over the molecular framework.³ For such a planar molecule, three geometries are possible, having the carbonyl and diazo functions either cis or trans relative to each other, about the C-C single bonds.



s-trans-s-trans



s-trans-s-cis



s-cis-s-cis

Based on e.s.r. studies of the carbene radical obtained through photolysis of the parentdibenzoyldiazomethane molecule, Murai, Torres and Strausz⁴ concluded that the s-trans-s-cis conformation was favored. In contrast, a study based on ¹H NMR and dipole measurements⁵ predicted the s-cis-s-cis conformation for a series of related, alkyl substituted analogues, $\text{RCOCN}_2\text{COR}'$ ($\text{R}, \text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3$). The structural determination of the title species was therefore necessary in order to unambiguously establish the molecular conformation.

In addition, the chemistry of diazoalkanes with metal complexes have been of interest in recent years owing to the tremendous diversity of this chemistry⁶ (see Chapter I). Diazoalkanes can react as 1,3 dipoles or as nucleophiles through either the carbon or the terminal nitrogen atom, producing a variety of metal species, some containing the intact diazoalkane molecule, while others have only fragments of the parent species (see Chapter I). Since part of these studies involved the chemistry of dibenzoyldiazomethane with transition metal complexes (see Chapter V), the structural determination of this diazoalkane molecule was of importance in order to form a basis for structural comparisons with the coordinated species and to assist in understanding the metal chemistry of this species. The X-ray structural determination of dibenzoyldiazomethane was therefore undertaken for the above reasons.

EXPERIMENTAL

Yellow crystals of dibenzoyldiazomethane, prepared by the reaction of $(\text{C}_6\text{H}_5\text{CO})_2\text{CH}_2$ with *p*-toluene sulfonylazide⁷ and recrystallized twice from ethanol were kindly supplied by Dr. M. Torres and Professor O.P. Strausz (University of Alberta). A suitable crystal was mounted in air on a glass fibre, and precautions were taken to minimize the exposure of the crystal to light, throughout the data collection.

Preliminary Weissenberg and precession photographs indicated the monoclinic space group P_{2_1}/c with systematic absences $h0\ell$, $\ell = 2n+1$ and $0k0$, $k = 2n+1$. However, owing to an unfavorable β angle (*ca.* 123°) the non-standard P_{2_1}/n setting with a somewhat more favorable β angle (118.18°) was chosen. The cell parameters are listed in Table 9 along with the pertinent crystal data and intensity collection details. Otherwise the data collection proceeded as outlined in Chapter II.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods, using the program MULTAN.⁸ The solution was based on 231 reflections having $|E| > 1.40$ and 1617 phase relationships. The E-map corresponding to the solution with the best figures of merit revealed the positions of the 15 carbon atom backbone. All other non-hydrogen atoms were located in a subsequent E-map obtained by recycling MULTAN.⁹ All hydrogen atoms were located in subse-

Table 9. Summary of Data and Intensity Collection for
Dibenzoyldiazomethane.

Compound	$(\text{C}_6\text{H}_5)\text{COCN}_2\text{CO}(\text{C}_6\text{H}_5)$
Formula	$\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_2$
Formula Weight	250.26
Cell Parameters	
a	9.5631(9) Å
b	14.5638(19) Å
c	10.1538(11) Å
β	118.184(9)°
V	1246.6 Å ³
Z	4
Density	1.333 g·cm ⁻³ (calcd.)
Space Group	$\text{C}_{2h}^5 - \text{P}_{21}/n$
Crystal Dimensions	0.432 x 0.357 x 0.084 mm
Crystal Volume	0.0130 mm ³
Crystal Shape	monoclinic prism with major faces of the form (010), (0 $\bar{1}$ 2), (01 $\bar{1}$)
Temperature	20°C
Radiation	Cu K α (λ = 1.540562 Å)
μ	7.015 cm ⁻¹
Takeoff Angle	2.75°
Scan Speed	2° in 2 θ /min
Scan Range	0.90° below K α_1 to 0.90° above K α_2
Background Counting Time	10 s (2 θ < 77.5°); 20 s (77.5° < 2 θ \leq 122.5°)
2 θ Limits	3.0° - 122.5°

Table 9, Continued

2 θ Limits for Centered Reflections	50.0° \leq 2 θ \leq 70.0°
Final Number of Parameters	172
Unique Data Collected	2010
Unique Data Used ($F_O^2 \geq 3\sigma(F_O^2)$)	1471
Error in Observation of Unit Weight	1.40 electrons
R	0.038
R _w	0.057

quent electron density difference maps. Full matrix least-squares refinement techniques were used, with atomic scattering factors from Cromer and Waber¹⁰ used for all atoms except hydrogen, for which the values from Stewart, Davidson and Simpson¹¹ were used. All non-hydrogen atoms were refined as individual atoms having anisotropic thermal parameters. The hydrogen atoms were included as fixed contributions in their idealized positions, with thermal parameters of 1 \AA^2 greater than the equivalent isotropic B for the corresponding carbon atom. Absorption corrections were not applied owing to the very small linear absorption coefficient (7.015 cm^{-1}). In the final electron density difference map, the top twenty residuals were less than 0.10 e/\AA^3 and were distributed randomly throughout space. In earlier difference maps, a typical H atom had a value of 0.47 e/\AA^3 . A more detailed discussion of the methods used in the structure solution and refinement is outlined in Chapter II.

RESULTS

A stereoview of the unit cell is presented in Figure 6. The crystallographic a axis is going into the page, the b axis runs from the bottom to the top, and the c axis goes from left to right across the diagram. Figure 7 (50% ellipsoids) shows the numbering scheme used in the molecule (hydrogens have the same number as their attached carbon atoms). The final positional and thermal parameters for the non-hydrogen atoms are in Table 10 and the idealized

positional and thermal parameters for the hydrogen atoms are given in Table 11. Relevant interatomic distances (bonded and non-bonded) are listed in Table 12, while bond angles and torsion angles are in Table 13. A listing of the observed and calculated structure amplitudes is available.¹²

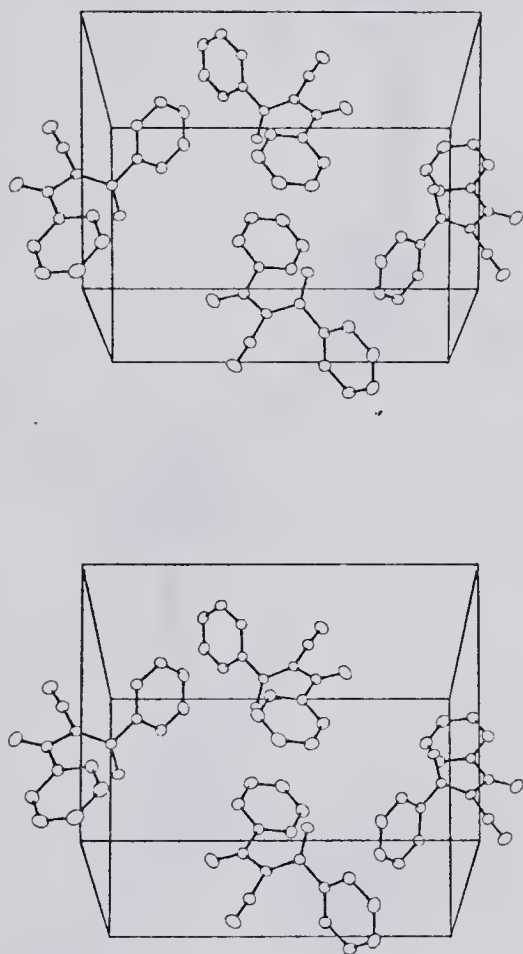


Figure 6. Cell Packing Diagram of $\text{PhCOCN}_2\text{COPh}$.

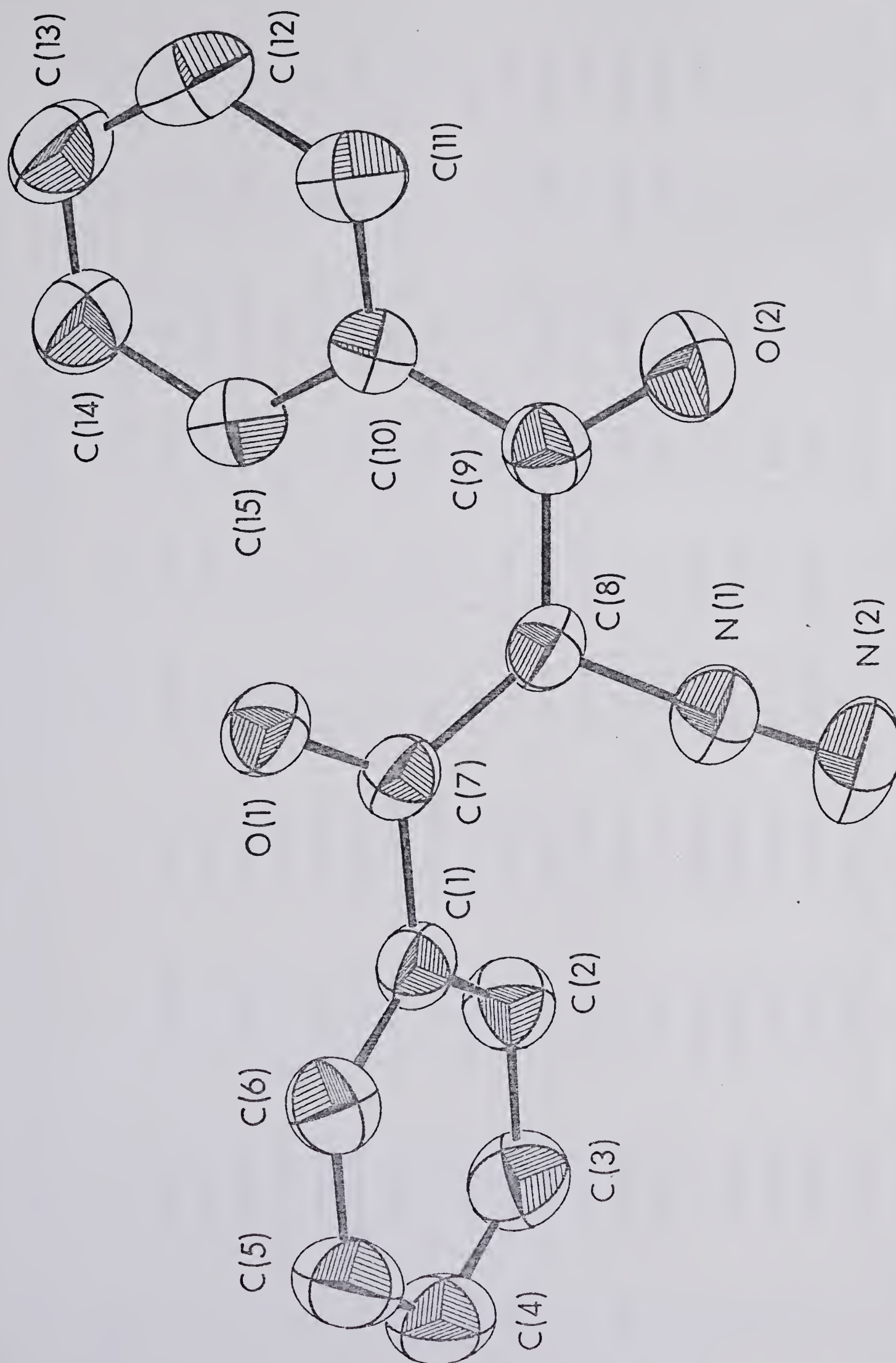


Figure 7. Perspective View of Dibenzo[diazomethane.

Table 10. Positional and Thermal Parameters for the Non-Hydrogen Atoms of [PhCOCN2COPh].

Atom	a			b			z	U ^b				
	x	y		U11	U22	U33		U12	U13	U23		
O(1)	0.6692(2)	1.06999(10)	0.6156(1)	5.85(9)	6.45(9)	3.77(7)	0.49(7)	0.42(6)	2.10(6)	0.42(6)		
O(2)	0.8448(2)	0.8184(1)	0.5629(2)	8.4(1)	4.87(9)	7.0(1)	1.18(8)	0.93(7)	2.55(8)	0.93(7)		
N(1)	0.6458(2)	0.9197(1)	0.3456(2)	6.4(1)	5.6(1)	4.48(9)	-0.21(9)	0.51(9)	2.26(8)	0.51(9)		
N(2)	0.5815(3)	0.8797(2)	0.2404(2)	10.1(2)	8.2(1)	5.3(1)	-1.3(1)	2.4(1)	2.4(1)	2.4(1)		
C(1)	0.5869(2)	1.1121(1)	0.3644(2)	3.9(1)	4.4(1)	3.94(9)	-0.60(8)	0.23(8)	1.40(8)	0.23(8)		
C(2)	0.6369(2)	1.1148(1)	0.2557(2)	5.1(1)	5.7(1)	4.8(1)	0.13(9)	0.01(9)	2.43(9)	0.01(9)		
C(3)	0.5662(3)	1.1753(2)	0.1366(2)	7.5(1)	6.1(1)	4.6(1)	-0.1(1)	0.5(1)	2.9(1)	0.5(1)		
C(4)	0.4449(3)	1.2313(2)	0.1235(2)	7.6(2)	5.0(1)	5.3(1)	0.0(1)	0.8(1)	1.9(1)	0.8(1)		
C(5)	0.3953(3)	1.2296(2)	0.2308(3)	6.0(1)	5.0(1)	7.2(1)	1.0(1)	0.5(1)	2.4(1)	0.5(1)		
C(6)	0.4674(2)	1.1714(1)	0.3522(2)	5.2(1)	4.8(1)	5.6(1)	0.16(9)	0.07(9)	2.69(10)	0.07(9)		
C(7)	0.6616(2)	1.0496(1)	0.4954(2)	3.6(1)	4.9(1)	3.81(9)	-0.37(8)	0.24(8)	1.38(8)	0.24(8)		
C(8)	0.7266(2)	0.9618(1)	0.4776(2)	4.8(1)	5.0(1)	3.41(9)	-0.19(9)	0.55(8)	1.45(8)	0.55(8)		
C(9)	0.8454(2)	0.9001(1)	0.5903(2)	5.2(1)	4.9(1)	4.9(1)	0.56(9)	0.04(9)	2.57(9)	0.04(9)		
C(10)	0.9681(2)	0.9398(1)	0.7333(2)	4.5(1)	5.2(1)	4.4(1)	0.80(9)	0.01(8)	2.05(9)	0.01(8)		
C(11)	1.0351(3)	0.8834(2)	0.8583(2)	5.8(1)	6.5(1)	5.6(1)	1.0(1)	1.0(1)	2.4(1)	1.0(1)		
C(12)	1.1530(3)	0.9166(2)	0.9923(2)	6.3(1)	10.0(2)	4.6(1)	1.5(1)	1.2(1)	1.7(1)	1.2(1)		
C(13)	1.2058(3)	1.0050(2)	1.0018(3)	5.1(1)	9.7(2)	5.5(1)	0.8(1)	-1.3(1)	0.9(1)	-1.3(1)		
C(14)	1.1429(3)	1.0610(2)	0.8779(3)	4.8(1)	7.0(1)	6.7(1)	-0.0(1)	-1.3(1)	1.5(1)	-1.3(1)		
C(15)	1.0231(2)	1.0289(1)	0.7440(2)	4.6(1)	5.6(1)	5.3(1)	0.6(1)	0.24(10)	1.73(9)	0.24(10)		

^a Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

^b The form of the thermal ellipsoid is: $\exp[-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^3$.

Table 11. Idealized Positional and Thermal Parameters for the Hydrogen Atoms of [PhCOCN2COPh].

Atom	x	y	z	B(A ²)	Atom	x	y	z	B(A ²)
H(2)	0.7191	1.0749	0.2632	5.04	H(11)	0.9999	0.8216	0.8515	5.81
H(3)	0.6017	1.1775	0.0636	5.81	H(12)	1.1984	0.8783	1.0781	6.81
H(4)	0.3953	1.2718	0.0405	6.09	H(13)	1.2857	1.0281	1.0944	6.86
H(5)	0.3114	1.2690	0.2217	6.00	H(14)	1.1819	1.1217	0.8844	6.23
H(6)	0.4351	1.1715	0.4276	5.09	H(15)	0.9785	1.0677	0.6589	5.25

Table 12. Selected Interatomic Distances (\AA) for $(\text{PhCO})_2\text{CN}_2$.

BONDED CONTACTS

N(1) - N(2)	1.112(2)	C(1) - C(2)	1.395(3)
N(1) - N(2)*	1.151(3)	C(2) - C(3)	1.387(3)
N(1) - C(8)	1.339(2)	C(3) - C(4)	1.372(3)
C(7) - O(1)	1.224(2)	C(4) - C(5)	1.379(3)
C(7) - O(1)*	1.240(2)	C(5) - C(6)	1.382(3)
C(9) - O(2)	1.221(2)	C(6) - C(1)	1.390(3)
C(9) - O(2)*	1.250(2)	C(10) - C(11)	1.389(3)
C(1) - C(7)	1.488(2)	C(11) - C(12)	1.381(3)
C(7) - C(8)	1.469(3)	C(12) - C(13)	1.370(4)
C(8) - C(9)	1.477(3)	C(13) - C(14)	1.377(3)
C(9) - C(10)	1.487(3)	C(14) - C(15)	1.382(3)
		C(15) - C(10)	1.384(3)

NON-BONDED CONTACTS

O(1) - C(6)	2.861(2)	C(7) - H(15)	2.694(2)
O(1) - C(15)	3.056(2)	C(8) - H(2)	2.704(2)
O(2) - H(11)	2.585(2)	C(8) - H(15)	2.717(2)
O(2) - H(3) ^a	2.597(1)	C(9) - H(6) ^d	2.802(2)
O(2) - C(11)	2.836(3)	C(10) - H(2) ^e	2.982(2)
N(1) - H(2)	2.618(2)	C(12) - H(3) ^e	2.993(3)
N(2) - H(3) ^b	2.861(2)	C(15) - H(2) ^e	2.922(2)
C(4) - H(15) ^c	2.949(2)		

* Bond lengths corrected for riding motion, where the second atom is riding on the first.

^a Atom located at position $1\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

^b Atom located at position $1-x, 2-y, -z$.

^c Atom located at position $-\frac{1}{2}+x, 2\frac{1}{2}-y, -\frac{1}{2}+z$.

^d Atom located at position $1-x, 2-y, 1-z$.

^e Atom located at position $2-x, 2-y, 1-z$.

Table 13. Selected Bond Angles (deg) for $(\text{PhCO})_2\text{CN}_2$.

BOND ANGLES

N(2)-N(1)-C(8)	175.8(2)	C(9)-C(10)-C(15)	122.5(2)
N(1)-C(8)-C(7)	116.4(2)	C(1)-C(2)-C(3)	120.0(2)
N(1)-C(8)-C(9)	111.4(2)	C(2)-C(3)-C(4)	120.2(2)
O(1)-C(7)-C(1)	121.3(2)	C(3)-C(4)-C(5)	120.2(2)
O(1)-C(7)-C(8)	120.3(2)	C(4)-C(5)-C(6)	120.1(2)
O(2)-C(9)-C(8)	119.9(2)	C(5)-C(6)-C(1)	120.2(2)
O(2)-C(9)-C(10)	121.2(2)	C(6)-C(1)-C(2)	119.1(2)
C(1)-C(7)-C(8)	118.4(2)	C(10)-C(11)-C(12)	120.2(2)
C(7)-C(8)-C(9)	130.5(2)	C(11)-C(12)-C(13)	120.0(2)
C(8)-C(9)-C(10)	118.8(2)	C(12)-C(13)-C(14)	120.4(2)
C(7)-C(1)-C(2)	121.7(2)	C(13)-C(14)-C(15)	120.0(2)
C(7)-C(1)-C(6)	119.2(2)	C(14)-C(15)-C(10)	120.2(2)
C(9)-C(10)-C(11)	118.2(2)	C(15)-C(10)-C(11)	119.2(2)

TORSION ANGLES

C(1)-C(7)-C(8)-N(1)	- 36.7
C(1)-C(7)-C(8)-C(9)	159.4(2)
O(1)-C(7)-C(8)-C(9)	- 20.7(3)
C(7)-C(8)-C(9)-O(2)	154.5(2)
C(7)-C(8)-C(9)-C(10)	- 27.9(3)
N(1)-C(8)-C(9)-C(10)	167.5(2)
O(2)-C(9)-C(10)-C(15)	148.2(2)
O(2)-C(9)-C(10)-C(11)	- 28.4(3)
C(8)-C(9)-C(10)-C(11)	154.1(2)
C(8)-C(9)-C(10)-C(15)	- 29.3(3)
C(2)-C(1)-C(7)-C(8)	- 30.4(3)
C(2)-C(1)-C(7)-O(1)	149.7(2)
C(6)-C(1)-C(7)-O(1)	- 28.4(3)
C(6)-C(1)-C(7)-C(8)	151.6(2)
O(2)-C(9)-C(8)-N(1)	- 10.0(3)
O(1)-C(7)-C(8)-N(1)	- 36.8(2)

DESCRIPTION OF STRUCTURE AND DISCUSSION

The unit cell of dibenzoyldiazomethane consists of four discrete molecules, with no unusually close intermolecular contacts. The molecule has an s-trans-s-cis configuration as initially proposed by Murai *et al*⁴ based on e.s.r. results, but is in conflict with the s-cis-s-cis geometry proposed for the related diazoalkanes $\text{RCO}\text{CN}_2\text{COR}'$ ($\text{R}, \text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3$) based on ^1H NMR spectra and dipole measurements.⁵ While there is likely some cis-trans isomerization in solution, it is unlikely from steric arguments, that the s-cis-s-cis geometry would dominate, except possibly for the smallest substituents (R, R'). In the present structure however, the s-trans-s-cis geometry is consistent with such steric arguments, in that the two bulky phenyl groups have minimal contacts. The third possible conformation, s-trans-s-trans, would also minimize non-bonded contacts and in this regard, would seem to be the preferred conformation. For the s-trans-s-trans geometry, two carbonyl groups would have to be in close contact, whereas for the observed s-trans-s-cis conformation, one carbonyl and the much larger phenyl group are in close proximity. The observed geometry must therefore result from electronic factors (*vide infra*).

In the title compound, the close contacts between the carbonyl group and the phenyl ring, a consequence of the

s-trans-s-cis geometry, result in significant deviations from planarity within the molecule. The molecule is twisted about the C(7)-C(8) and C(8)-C(9) bonds such that O(1) is thrust above the diazomethylene plane while O(2) falls below this plane. The resulting O(1)-C(7)-C(8)-N(1) and O(2)-C(9)-C(8)-N(1) torsion angles are $-36.8(2)^\circ$ and $-10.0(3)^\circ$, respectively. These molecular twists oppose the tendency for the diazo and ketone groups to be coplanar³ and therefore reduce the π -delocalization somewhat. A tendency to maximize the delocalization probably keeps the molecule from deviating even more from planarity. Significantly, the cis carbonyl group (C(9)-O(2)) is twisted only 10° from the diazo group while the trans carbonyl (C(7)-O(1)) is twisted by *ca.* 37° . The latter group is the one interacting with the phenyl ring of the other benzoyl moiety in the present conformation. The two phenyl rings are also twisted by *ca.* 29° from the carbonyl groups, such that ring 1 (C(1)-C(6)) avoids the diazo group and ring 2 (C(10)-C(15)) avoids the carbonyl C(7)-O(1). This twisting also serves to reduce the possible delocalization over the molecular framework.

The C-C distances within both phenyl groups (average $1.385(8)$ and $1.381(6)$ Å) are somewhat shorter than in benzene and its derivatives,¹³ but these values not unexpected from the thermal vibrations of the rings. Consistent with this argument, the shortest C-C distances occur at the far

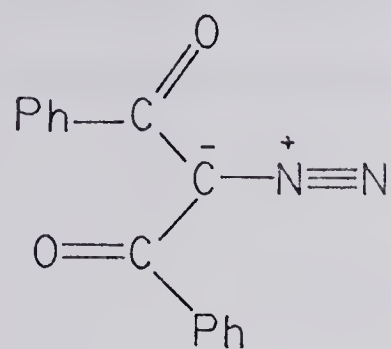
ends of the molecule (C(3),C(4),C(5) and C(12),C(13), C(14)) where the thermal motion is greatest. The C(1)-C(7) and C(9)-C(10) distances (1.488(2) and 1.487(3) Å, respectively) are in excellent agreement and correspond to normal C-C single bonds between sp^2 hybridized carbon atoms.¹⁴ On the other hand the C(7)-C(8) and C(8)-C(9) distances (1.469(3) and 1.477(3) Å, respectively) are somewhat shorter, indicating partial double bond character. Both carbonyl C-O distances (1.224(2) for C(7)-O(1) and 1.221(2) Å for C(9)-O(2)) are in good agreement with each other and indicate normal C=O double bonds.¹⁵ If these bond lengths are corrected for riding motion however, the corrected values (1.240(2) and 1.250(2) Å, respectively) indicate a bond order somewhat less than two, resulting from delocalization within the molecule. These corrected values may offer a better description of the carbonyl groups since they take the thermal vibrations of these groups into account.

Within the diazomethylene part of the molecule, the C-N-N angle is virtually linear (175.8(2)°), the C-N bond length (1.339(2) Å) indicates a partial double bond¹⁶ and the N-N bond distance (1.112(2) Å) is very close to the triple bond values observed in dinitrogen and aromatic diazonium compounds (1.097-1.098 Å).^{17,18} All three parameters agree well with the values reported for the six other diazoalkane molecules (C-N bond range 1.31-1.37 Å; N-N bond range 1.10-1.126 Å; N-N-C angle range 177°-180°).¹⁹⁻²⁴

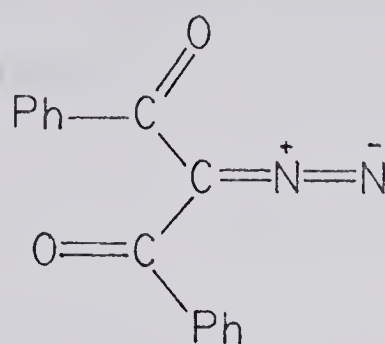
However, owing to thermal vibration, the N-N distance will be artificially short when an individual atom treatment is used and uncorrected values are not really meaningful. For this reason we prefer to rely on the riding motion corrected value. This value for the N-N distance ($1.151(3) \text{ \AA}$) is intermediate between a double and a triple bond,²⁵ consistent with the partial double bond character of the C-N bond, and again, indicates the electron delocalization within the molecule.

In order to establish the preference of the s-trans-s-cis conformation over the sterically favored s-trans-s-trans geometry, it is worthwhile considering some of the canonical forms possible for the molecule in the favored conformation, as shown in Figure 8. As mentioned previously, significant delocalization over the molecular framework is possible if all atoms are coplanar,³ and this is clearly seen from the canonical forms in Figure 8. The planarity of the molecule is opposed, however, by steric interactions which tend to suggest instead that the s-trans-s-trans conformation is most likely. However the average structure 8e indicates an electrostatic stabilization for the observed conformation. This interaction results from the positive charge on N(1) and the negative charge on O(2). Consistent with this argument, the torsion angle involving the carbonyl cis to the diazo group, O(2)-C(9)-C(8)-N(1), is only 10° whereas for the trans carbonyl, where there is no such

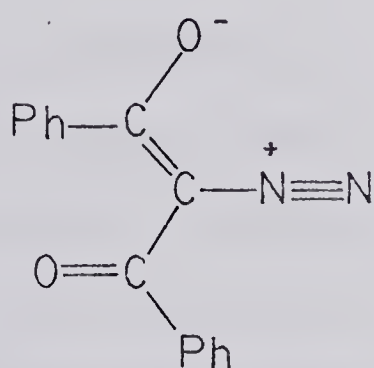
Figure 8. Major Canonical Forms for the s-trans-s-cis Conformation of $\text{PhCOCN}_2\text{COPh}$.



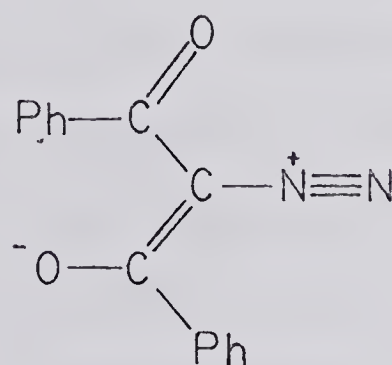
a



b

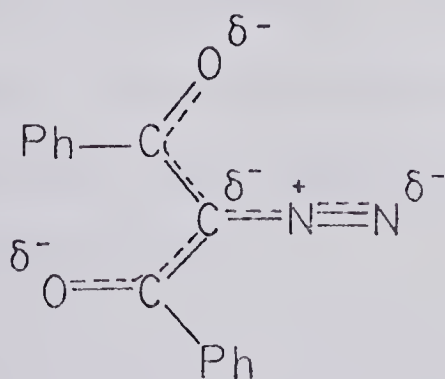


c



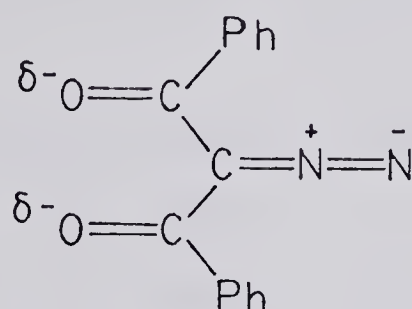
d

Average Electron Density Distribution



e

stabilizing electrostatic attraction, the torsion angle, $O(1)-C(7)-C(8)-N(1)$, is 37° . For an s-trans-s-trans geometry, there would be no attractive interactions possible between carbonyl and diazo groups, and in fact a destabilizing, repulsive interaction would result between the two carbonyl groups, as illustrated below.



Electrostatically, the s-cis-s-cis conformation is favored, whereas based on steric arguments, the s-trans-s-trans geometry is most likely. The observed s-trans-s-cis geometry is therefore a compromise between the electrostatic and steric forces within the molecule. The molecular parameters indicate that, in spite of the significant deviations from planarity, there is significant delocalization over the molecular framework. It should also be noted that the thermally corrected diazo and carbonyl bond lengths are those that are most chemically reasonable, giving the expected bond orders.

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Chapter IV.

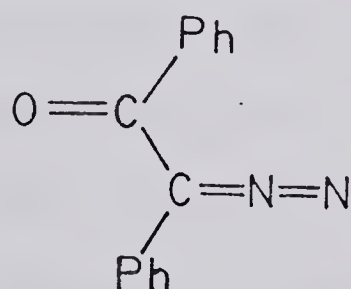
The Structure of Benzoylphenyldiazomethane.

INTRODUCTION

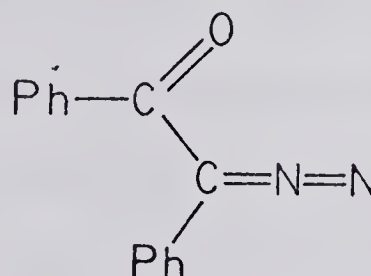
The e.s.r. spectrum of benzoylphenyldiazomethane, commonly known as azibenzil, has been reported by Murai, Torres and Strausz.¹ These authors noted that photolysis of a microcrystalline sample of PhCOCN_2Ph at 77°K resulted in a complex e.s.r. spectrum, consisting of a strong and a weak triplet signal and a quintet signal. The strong triplet was assigned to the trans conformer of the benzoylphenylmethylene radical, which is formed through loss of N_2 from the starting diazoalkane molecule, also assumed to have the trans geometry in the solid state. The weak triplet was assigned to the presence of small amounts of the cis conformer of this radical, and the novel quintet state was attributed to a triplet-triplet radical pair formed by the pairwise interaction of two triplet state benzoylphenylmethylene radicals, each having a trans conformation. For such a radical pair to form, two radicals must be in close proximity in the crystal lattice, which could result if, in a crystal sample of the parent diazoalkane species, two molecules were oriented such that there were close interactions between the diazo functions. Since benzoylphenyldiazomethane forms a relatively stable crystalline product, similar to the related species $(\text{PhCO})_2\text{CN}_2$ discussed

in Chapter III, a structural determination was undertaken to determine the intermolecular interactions within the unit cell in order to further understand the e.s.r. spectrum and to confirm the proposed trans geometry of the molecule.

Semiempirical CNDO/2 calculations² on benzoylphenyldiazomethane indicate that two geometries are preferred, having the carbonyl and diazo groups either cis or trans across the single bond, and having an essentially planar molecular framework. Other conformations resulting from rotations about the C-C bond were not favored.



trans



cis

However, the electric dipole moment measurements³ are compatible with either two cis-trans conformers in equilibrium or with only a single skewed conformer. Therefore the structure of PhCOCN_2Ph is also of interest for comparison with the results of the theoretical calculations.

In addition, the structural determination of benzoylphenyldiazomethane is of interest in relation to the structure of dibenzoyldiazomethane discussed in Chapter III. Few diazoalkane molecules have been structurally characterized⁴⁻⁹ and in none of these reports have the structures been discussed in terms of thermally corrected bond lengths. We maintain that when the atoms are undergoing significant thermal vibration, as is often the case at room temperature, the thermally corrected bond lengths are often more meaningful than the uncorrected values obtained from the least squares analysis. This is clear in previous structures of diazoalkane molecules⁴⁻⁹ where the C-N bond lengths indicated bond orders of *ca.* 1.5, whereas the corresponding N-N bond lengths were abnormally short, corresponding to bond orders close to 3, rather than the expected 2.5. We believe that this N-N bond shortening is a consequence of thermal vibration rather than increased N-N bond order as has previously been implied.⁴ The suitably corrected structural parameters of PhCOCN_2Ph , are therefore important for comparison with the parameters of $(\text{PhCO})_2\text{CN}_2$, which have been handled in an analogous manner, to help establish structural and chemical trends within diazoalkane molecules.

EXPERIMENTAL

Orange needles of benzoylphenyldiazomethane recrystallized from ether, were kindly supplied by Dr. M. Torres

and Professor O.P. Strausz (University of Alberta). A suitable crystal fragment, cut from one of the needles, was mounted in the air on a glass fibre. Preliminary film data showed Laue symmetry mmm with systematic absences $(h00, h = 2n+1; 0k0, k = 2n+1; 00l, l = 2n+1)$ consistent with the space group $P2_12_12_1$. The cell parameters, along with the pertinent crystal data and intensity collection details are listed in Table 14. Otherwise the data collection proceeded as outlined in Chapter II.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using the program MULTAN.¹⁰ The solution was based on 300 reflections having $|E| > 1.03$ and 2000 phase relationships. The E-map corresponding to the solution with the best combined figure of merit yielded the positions of all non-hydrogen atoms. All hydrogen atoms were found in a subsequent electron density difference map phased on the heavier atom framework. Full matrix least-squares techniques were used, with atomic scattering factors from Cromer and Waber¹¹ used for all atoms except hydrogen, for which the values from Stewart, Davidson and Simpson¹² were used. Anomalous dispersion terms for O, N and C were included in F_c . All non-hydrogen atoms were refined as individual atoms, with the phenyl carbon atoms having isotropic thermal parameters, and the rest having anisotropic thermal parameters. The hydrogen atoms were included as fixed contributions in

Table 14. Summary of Data and Intensity Collection for
Benzoylphenyldiazomethane.

Compound	$(\text{C}_6\text{H}_5)\text{COCN}_2(\text{C}_6\text{H}_5)$
Formula	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}$
Formula Weight	222.25
Cell Parameters	
a	5.600 (1) Å
b	13.347 (2) Å
c	15.018 (3) Å
V	1122.5
Z	4
Density	1.315 g·cm ⁻³ (calcd.) 1.30 (1) g·cm ⁻³ (exptl., floatation)
Space Group	$D_2^4 - P2_12_12_1$
Crystal Dimensions	0.384 x 0.216 x 0.129 mm
Crystal Volume	0.0107 mm ³
Crystal Shape	orthorhombic prism with faces $0\bar{1}\bar{1}$, 011, $0\bar{1}2$, $01\bar{2}$, 100, $\bar{1}00$
Temperature	20°C
Radiation	Cu Kα ($\lambda = 1.540562$ Å)
μ	6.447 cm ⁻¹
Receiving Aperture	4mm x 4mm; 30 cm from the crystal
Takeoff Angle	5.50°
Scan Speed	2° in 20/min
Scan Range	1.0° below $K\alpha_1$ to 1.0° above $K\alpha_2$
Background Counting Time	20 s

Table 14, Continued

2 θ Limits	3.0° - 123°
2 θ Limits for Centered Reflections	50.0° \leq 2 θ \leq 70°
Final Number of Parameters	94
Unique Data Collected	1068
Unique Data Used ($F_O^2 \geq 3\sigma(F_O^2)$)	888
Error in Observation of Unit Weight	1.979 electrons
R	0.052
R _w	0.070

their idealized positions, with thermal parameters of 1 \AA^2 greater than the equivalent isotropic B for the corresponding carbon atom. Absorption corrections were not applied owing to the very small magnitude of the linear absorption coefficient (6.447 cm^{-1}). In the final electron density difference map, the top twenty residuals ranged from 0.31 to 0.14 e/\AA^3 , and were in the vicinity of the two phenyl rings. In earlier difference Fourier maps, a typical hydrogen atom had an electron density of about 0.27 e/\AA^3 . For a more detailed discussion of structure solution techniques, the reader is referred to Chapter II.

RESULTS

A stereoview of the unit cell is shown in Figure 9. The crystallographic a axis goes into the page, the b axis runs from top to bottom and the c axis is from right to left. Figure 10 (50% ellipsoids) indicates the numbering scheme used within the molecule (hydrogen atoms have the same number as their attached carbon atoms). The final positional and thermal parameters for the non-hydrogen atoms are listed in Table 15 and the idealized positional and thermal parameters for the hydrogen atoms are given in Table 16. Selected interatomic distances are listed in Table 17, while bond angles and torsion angles are presented in Table 18. The least squares plane calculations are recorded in Table 19. A listing of the observed and calculated structure amplitudes is available.¹³

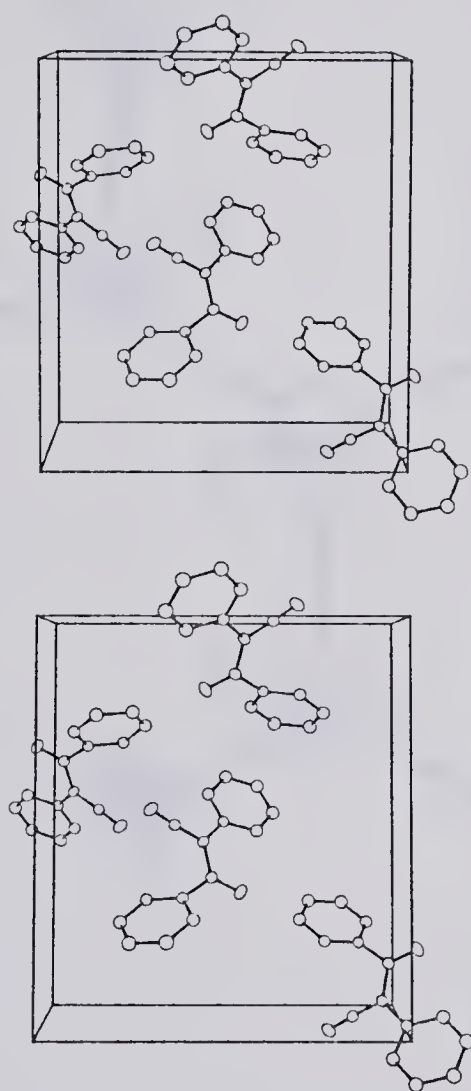


Figure 9.. 'Cell Packing Diagram of PhCOCN₂Ph.

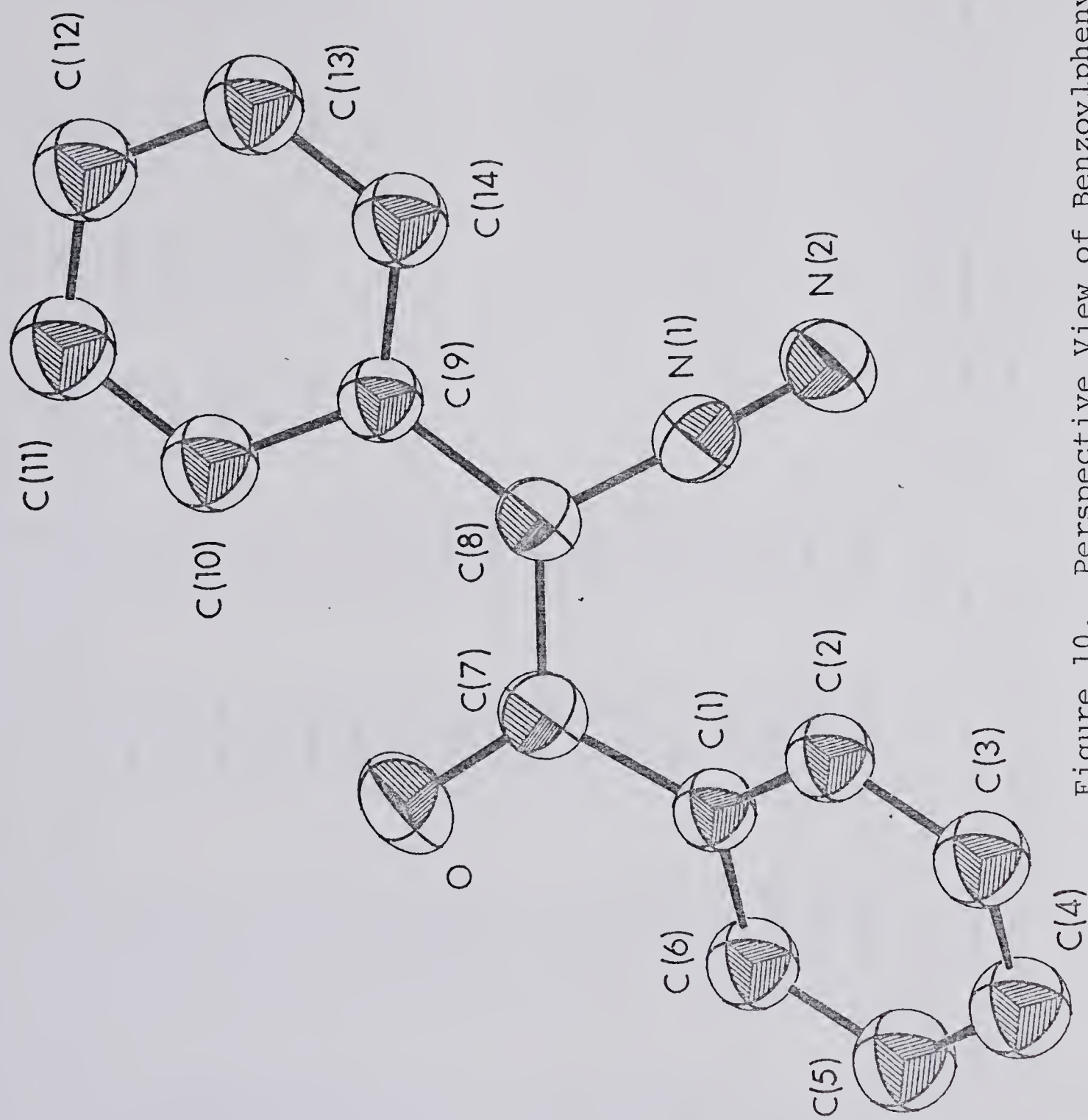


Figure 10. Perspective View of Benzoyldiazomethane.

Table 15. Positional and Thermal Parameters For the Non-Hydrogen Atoms of [PhCOCN2Ph].

Atom	^a			z	^b			U22	U33	U12	U13	U23
	x	y			U11							
O	0.4289(7)	0.5492(2)		0.6751(2)	8.4(2)			4.6(2)	6.8(2)	-1.4(2)	1.8(2)	-1.5(2)
N(1)	0.4459(7)	0.3658(2)		0.5107(2)	5.4(2)			4.3(2)	4.6(2)	-0.4(2)	0.3(2)	0.2(2)
N(2)	0.3788(8)	0.3005(3)		0.4698(2)	7.3(3)			5.5(2)	5.8(2)	-1.3(2)	0.5(2)	-1.3(2)
C(7)	0.4017(8)	0.4677(3)		0.6379(3)	4.8(2)			3.6(2)	5.2(2)	0.1(2)	0.1(2)	-0.1(2)
C(8)	0.5268(8)	0.4447(3)		0.5552(3)	5.2(3)			3.4(2)	4.4(2)	-0.2(2)	0.2(2)	-0.2(2)
C(1)	0.2444(7)	0.3909(3)		0.6795(2)	0.51(1)							
C(2)	0.3141(8)	0.2906(3)		0.6874(3)	3.65(8)							
C(3)	0.1689(9)	0.2232(3)		0.7328(3)	4.36(9)							
C(4)	-0.043(1)	0.2540(3)		0.7685(3)	4.8(1)							
C(5)	-0.1113(9)	0.3538(4)		0.7615(3)	4.9(1)							
C(6)	0.0323(9)	0.4214(3)		0.7184(3)	3.98(9)							
C(9)	0.7246(8)	0.5007(3)		0.5126(3)	3.36(8)							
C(10)	0.7805(9)	0.5975(3)		0.5381(3)	4.38(9)							
C(11)	0.972(1)	0.6464(4)		0.4985(3)	5.0(1)							
C(12)	1.102(1)	0.6020(3)		0.4324(3)	4.8(1)							
C(13)	1.0466(9)	0.5068(3)		0.4058(3)	4.57(9)							
C(14)	0.8591(9)	0.4564(3)		0.4464(3)	4.21(9)							

^a

Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

^bThe form of the thermal ellipsoid is: $\exp[-2^*PI^2(a^*U11h^2+b^*U22k^2+c^*U33l^2+2a^*b^*U12hk+2a^*c^*U13hl+2b^*c^*U23kl)]$. The quantities given in the table are the thermal coefficients $\times 10^3$. Isotropic $B(A^2)$.

Table 16. Idealized Positional and Thermal Parameters For the Hydrogen Atoms of [PhCOCN2Ph].

Atom	x	y	z	B(A ²)	Atom	x	y	z	B(A ²)
H(2)	0.4602	0.2686	0.6619	4.65	H(10)	0.6882	0.6304	0.5824	5.38
H(3)	0.2176	0.1554	0.7392	5.36	H(11)	1.0135	0.7120	0.5177	5.99
H(4)	-0.1437	0.2072	0.7979	5.80	H(12)	1.2307	0.6370	0.4051	5.84
H(5)	-0.2580	0.3753	0.7868	5.93	H(13)	1.1358	0.4754	0.3598	5.58
H(6)	-0.0140	0.4898	0.7151	4.98	H(14)	0.8225	0.3900	0.4282	5.21

Table 17. Selected Interatomic Distances (\AA) for PhCOCN_2Ph .

BONDED CONTACTS

N(1)-N(2)	1.130(5)	C(3)-C(4)	1.365(7)
N(1)-N(2)*	1.151(5)	C(4)-C(5)	1.390(7)
N(1)-C(8)	1.328(5)	C(5)-C(6)	1.372(6)
C(7)-O	1.231(4)	C(6)-C(1)	1.385(6)
C(7)-O*	1.257(5)	C(9)-C(10)	1.383(6)
C(1)-C(7)	1.489(5)	C(10)-C(11)	1.390(7)
C(7)-C(8)	1.459(6)	C(11)-C(12)	1.367(7)
C(8)-C(9)	1.482(6)	C(12)-C(13)	1.367(6)
C(1)-C(2)	1.399(5)	C(13)-C(14)	1.389(7)
C(2)-C(3)	1.391(6)	C(14)-C(9)	1.381(6)

NON-BONDED CONTACTS

O-H(10)	2.285(3)	C(8)-H(14)	2.630(4)
O-C(6)	2.874(5)	C(8)-H(10)	2.669(4)
O-C(10)	2.920(6)	C(3)-H(14) ^a	2.978(5)
N(1)-H(14)	2.467(4)	C(12)-H(5) ^e	2.931(5)
N(1)-H(2)	2.617(3)	C(13)-H(5) ^e	2.877(5)
N(1)-C(14)	2.783(6)	C(13)-N(1) ^d	3.320(6)
N(2)-N(2) ^{a,b}	3.238(4)	C(13)-N(2) ^d	3.459(6)
N(2)-N(1) ^a	3.300(6)	H(14)-C(2) ^b	2.971(4)
C(7)-H(6)	2.617(4)	H(14)-C(3) ^b	2.978(5)
C(7)-H(2)	2.702(4)	O-C(8) ^c	5.541(6)
C(8)-C(8) ^{a,b}	6.133(6)	O-C(8) ^f	6.254(5)
C(8)-C(8) ^{c,d}	5.600(1)		

* Bond lengths corrected for riding motion, where the second atom is riding on the first.

^a Atom is located at the position $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

^b Atom is located at the position $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.

^c Atom is located at the position $-1+x, y, z$.

^d Atom is located at the position $1+x, y, z$.

^e Atom is located at the position $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$.

^f Atom is located at the position $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$.

Table 18. Selected Angles (deg) for PhCOCN₂Ph.

BOND ANGLES

N(2)-N(1)-C(8)	177.3(4)	C(1)-C(2)-C(3)	119.8(4)
N(1)-C(8)-C(7)	115.6(4)	C(2)-C(3)-C(4)	120.4(4)
N(1)-C(8)-C(9)	116.0(4)	C(3)-C(4)-C(5)	119.8(5)
O-C(7)-C(8)	120.8(4)	C(4)-C(5)-C(6)	120.3(5)
O-C(7)-C(1)	119.4(4)	C(5)-C(6)-C(1)	120.5(4)
C(1)-C(7)-C(8)	119.7(3)	C(6)-C(1)-C(2)	119.0(4)
C(7)-C(8)-C(9)	128.4(3)	C(9)-C(10)-C(11)	119.6(4)
C(7)-C(1)-C(2)	122.0(4)	C(10)-C(11)-C(12)	121.3(4)
C(7)-C(1)-C(6)	118.7(3)	C(11)-C(12)-C(13)	119.6(5)
C(8)-C(9)-C(10)	121.4(4)	C(12)-C(13)-C(14)	119.7(5)
C(8)-C(9)-C(14)	120.2(4)	C(13)-C(14)-C(9)	121.4(4)
		C(14)-C(9)-C(10)	118.5(4)

TORSION ANGLES

C(1)-C(7)-C(8)-N(1)	16.3(6)
C(1)-C(7)-C(8)-C(9)	-166.8(4)
O-C(7)-C(8)-C(9)	11.4(7)
O-C(7)-C(8)-N(1)	14.5(4)
C(7)-C(8)-N(1)-N(2)	143(10)
C(10)-C(9)-C(8)-N(1)	-18.1(4)
C(2)-C(1)-C(7)-O	46.3(4)

Table 19. Least Squares Plane Calculations.^a

plane no.	equation
1	$-0.6487X + 0.5856Y - 0.4861Z + 2.4715 = 0$
2	$-0.7752X + 0.3628Y - 0.5171Z + 4.4422 = 0$
3	$-0.4739X - 0.2080Y - 0.8557Z + 10.4751 = 0$
4	$-0.6247X + 0.3666Y - 0.6894Z + 5.3887 = 0$

Deviations from the Planes (\AA)
Plane no.

Atom	1	2	3	4
O	0.277(3) ^b	-0.003(3)		
N(1)	-0.017(4)			
N(2)	0.015(4)			
C(1)		-0.003(4)	0.010(4)	
C(2)			0.001(4)	
C(3)			-0.010(5)	
C(4)			0.009(5)	
C(5)			0.002(5)	
C(6)			0.012(4)	
C(7)	0.011(4)	0.009(4)	-0.087(4) ^b	
C(8)	-0.019(4)	-0.003(4)		-0.026(4) ^b
C(9)	0.011(4)			-0.004(4)
C(10)				0.011(5)
C(11)				-0.010(5)
C(12)				0.002(5)
C(13)				0.006(5)
C(14)				-0.005(5)

Dihedral Angles Between Planes

Plane A	Plane B	angle(deg)
1	2	14.8
1	3	53.0
1	4	17.2
2	3	42.7
2	4	13.1
3	4	35.9

^aX, Y, and Z are the orthogonal coordinates (\AA) with X along the a axis, Y in the (a-b) plane and Z along the c^{*} axis.

^bNot included in the least squares plane calculation.

DESCRIPTION OF STRUCTURE AND DISCUSSION

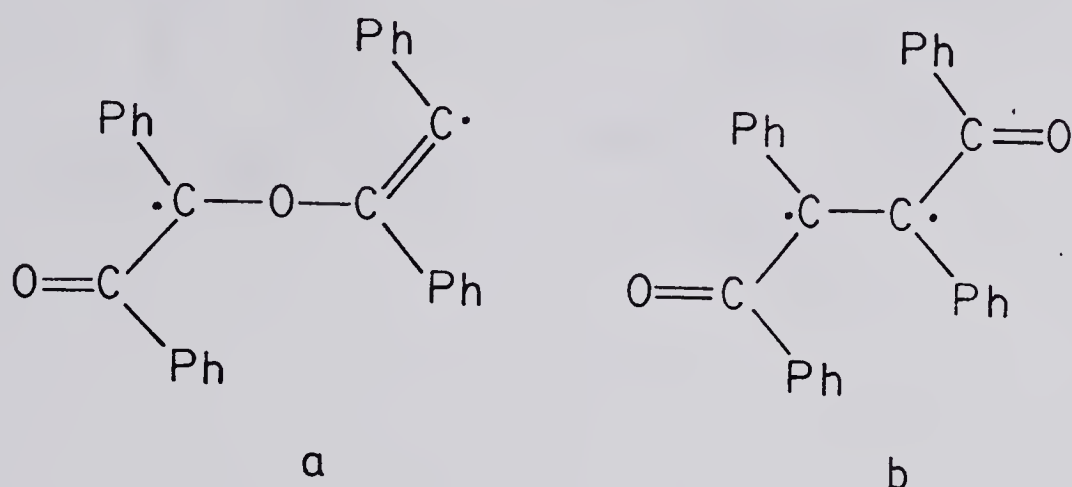
Within the unit cell of benzoylphenyldiazomethane there are four discrete molecules. Figure 9 indicates that these molecules can be grouped in pairs along the crystallographic screw axis in the x -direction. In this arrangement the molecules have their diazomethylene groups directed towards each other but inclined somewhat along a such that zig-zag arrays of diazomethylene groups, parallel to the a axis, result. These diazomethylene groups therefore come into rather close contact, and the N(2)-N(2) distance along the zig-zag chain is $3.238(4) \text{ \AA}$. Although it is difficult to establish a normal van der Waals contact for such an interaction, this contact can be related to the radius of an aromatic ring (1.85 \AA).¹⁴ It is not unreasonable to assume that the π system of the diazomethylene function is similar to that of an aromatic ring, and thus we estimate that a normal non-bonded contact between two diazo functions is approximately 3.70 \AA . As such, the N(2)-N(2) distance in the present structure indicates a significant interaction between the two diazomethylene groups.

In the e.s.r. study by Strausz and coworkers,¹ photolysis of a microcrystalline sample of the title compound at 77°K resulted in the production of the benzoylphenylmethylene radical. Since the elimination of N_2 at this temperature in the solid state is not expected to change

the geometry of the molecule, the cell packing diagram shown in Figure 9 should be representative of the orientation of the radicals after photolysis and should prove useful in interpreting the e.s.r. results. Initially, the e.s.r. spectrum showed a strong triplet signal (assigned to the trans configuration of the benzoylphenylmethylen radical), a weak triplet signal (assigned to the cis configuration of this group) and a quintet signal. The quintet signal was thought to arise from the pairwise interaction of two neighboring triplet radicals.¹ Within the unit cell of benzoylphenyldiazoalkane, there are two close contacts between neighboring carbene carbon atoms which could give rise to this interaction. The first is along the zig-zag chain, where the C(8)-C(8) separation is $6.133(6) \text{ \AA}$, and the second occurs between molecules separated by one unit cell translation in a , in which the C(8)-C(8) distance is $5.600(1) \text{ \AA}$. Both possibilities are consistent with the separation expected between radical pairs producing the quintet signal, as indicated by the zero field splitting parameter, $D(0.0943 \text{ cm}^{-1})$,¹ which is a function of the separation of unpaired electrons in the radicals.

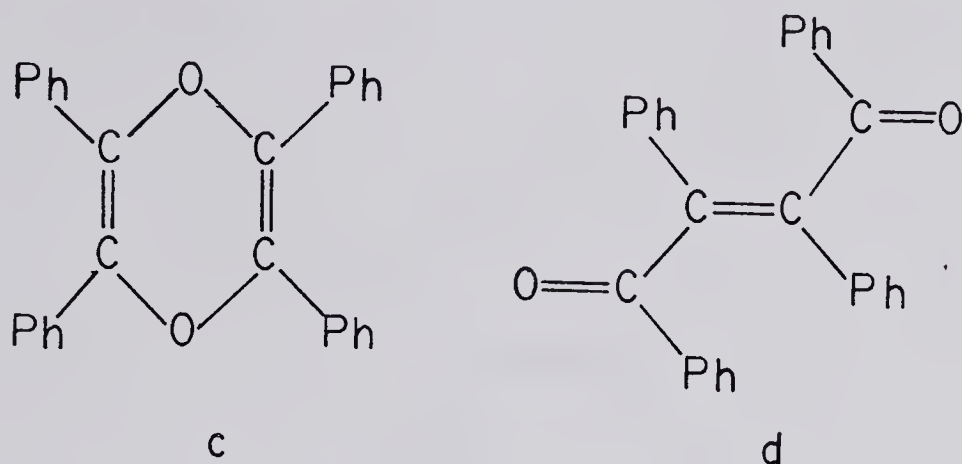
Upon warming the benzoylphenylmethylen radical from 77°K to 90°K , the quintet signal decays to a new triplet signal which was postulated to result from the formation of a diradical through inversion and a single, covalent bond formation.¹ This new triplet signal, which decays

above 120°K could result from a covalent bond formed between the carbene carbon atom of one molecule and a carbonyl linkage of another (as in (a), below), or between the carbene atoms of two adjacent molecules, resulting in (b).¹⁵



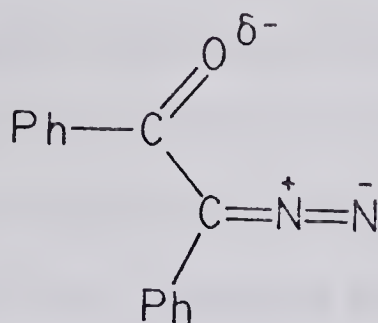
The closest contacts of type (a) occur between molecules separated by one cell translation along the a axis, where the C(8)-O distance is 5.541(6) Å. The next closest such interaction is 6.254(5) Å (see Table 17). The two closest interatomic distances between carbene atoms C(8)-C(8) are 5.600(1) and 6.133(6) Å (*vide supra*). It is not possible to determine which bond formation is most likely from the structural data. However, if a C(8)-O bond is formed, the decay of the triplet signal (above 120°K) may result from rearrangement of the molecule and formation of another bond, resulting in (c).¹⁵ In the case of a

C(8)-C(8) bond formation, this decay could result from a rotation about the C(8)-C(8) bond, with the subsequent formation of a C=C double bond, as in (d).¹⁵



Within the molecule, the carbonyl and diazo groups are trans to each other across the C-C single bond, as expected from the e.s.r. results.¹ This geometry and the cis conformation are the two which are favored owing to π -delocalization within the molecule, and theoretical calculations² on benzoylphenyldiazomethane have confirmed this. The preference of one of these two conformations over the other is dependent on several factors, as discussed in Chapter III. For optimum delocalization of the π electrons, the whole molecular fragment should be planar.¹⁶ This planarity is opposed by steric interactions, the greatest of which occurs between the two phenyl groups in the cis configuration. Thus, the two phenyl rings cannot both be coplanar with the carbonyl and diazo groups, and delocaliz-

ation through the phenyl rings is lost in this conformation. However, as shown in Chapter III, the cis conformation is stabilized by an electrostatic attraction between the carbonyl and diazo functions, which is not possible in a trans geometry.



Which of the two preferred conformations is favored will depend on which of the above stabilizing or destabilizing forces predominate. In the present compound, the observed trans geometry implies that the steric repulsion between the two phenyl groups predominate, and thus the trans configuration is preferred. It is also possible that the observed trans conformer may be favored in the present structure by packing considerations.

In the trans conformation, the molecule is most stable when it is completely planar, owing to the possibility of π -delocalization.¹⁶ However, in the present structure, the molecule is not totally planar, but is skewed somewhat. For example, the O-C(7)-C(8)-N(1) torsion angle is $14.5(4)^\circ$

and the torsion angle between phenyl ring 2 and the diazomethane group (C(10)-C(9)-C(8)-N(1)) is $-18.1(4)^\circ$. These two values indicate that some conjugation is possible between the carbonyl and diazo group and between the diazo group and the adjacent phenyl ring. On the other hand the C(1)-C(6) phenyl ring is twisted considerably from the adjacent carbonyl group (torsion angle C(2)-C(1)-C(7)-O = $46.3(4)^\circ$), allowing very little electron delocalization between this phenyl and the carbonyl group. This twisting probably results from steric interactions between the phenyl ring and the diazo and carbonyl groups, with the phenyl rings skewing to avoid contacts with these groups.

The C-C distances within ring 1 (C(1)-C(6), average $1.384(12) \text{ \AA}$) and ring 2 (C(9)-C(14), average $1.378(8) \text{ \AA}$), analogous to those in dibenzoyldiazomethane, are somewhat shorter than the values found in benzene and its derivatives.¹⁷ Again, this is consistent with the thermal vibrations of the rings, with the shortest C-C distances occurring at the C(4) and C(12) ends of the rings, where the thermal motion is the greatest. The C(1)-C(7) and C(8)-C(9) distances ($1.489(5)$ and $1.482(6) \text{ \AA}$) agree well with the predicted value for a single bond between sp^2 hybridized carbon atoms,¹⁴ indicating that there is little actual delocalization between either of the phenyl rings and the carbonyl-diazo backbone, even though some conjugation is possible between ring 2 and the diazo group (*vide supra*). The C(7)-

C(8) bond length ($1.459(6) \text{ \AA}$), on the other hand, is intermediate between a single and double bond,¹⁴ and suggests significant conjugation between the carbonyl and diazo functions. In dibenzoyldiazomethane, the corresponding bond lengths ($1.469(3)$ and $1.477(3) \text{ \AA}$) are somewhat longer than in the present structure, although not significantly. In addition, the carbonyl C(7)-O distance in the present structure ($1.231(4) \text{ \AA}$) although not significantly different from the two carbonyls in $(\text{PhCO})_2\text{CN}_2$ ($1.224(2)$ and $1.221(2) \text{ \AA}$), is still somewhat longer. Although the differences for the C-C and C-O bond lengths between the mono and dibenzoyl compounds are not significant, taken together, they are consistent with a somewhat higher degree of conjugation between the diazo and carbonyl groups in the present structure, possibly because the delocalization occurs over one carbonyl group in PhCOCN_2Ph , and over two in $(\text{PhCO})_2\text{CN}_2$. A riding motion correction of the C-O bond yields a value of $1.257(5) \text{ \AA}$, which indicates a bond order somewhat less than two.¹⁸

The diazomethylene fragment of the present structure is virtually linear ($177.3(4)^\circ$), as expected. The N(1)-N(2) (uncorrected) bond length ($1.130(5) \text{ \AA}$) is somewhat longer than in the other reported diazoalkane structures,⁴⁻⁹ where a range of $1.10(2) - 1.126(4) \text{ \AA}$ was observed. The N-N bond length corrected for riding motion ($1.151(5) \text{ \AA}$) is in excellent agreement with the analogous thermally corrected

distance in dibenzoyldiazomethane ($1.151(3) \text{ \AA}$) and indicates a bond order of *ca.* 2.5.¹⁹ Again, the corrected bond distance is believed to be a better indication of the true bond length, since thermal motion is taken into account. Furthermore, this corrected distance corresponds to the expected N-N bond order. The C(8)-N(1) bond length of $1.328(5) \text{ \AA}$ is somewhat shorter than the corresponding value in dibenzoyldiazomethane ($1.339(2) \text{ \AA}$), and is intermediate between a single and double bond.²⁰ The N-N and C-N bond distances are consistent with a significant amount of π -delocalization within the diazomethylene group, and again suggest that the delocalization in the present structure is somewhat greater than in the dibenzoyl species.

Overall, these structural parameters of benzoylphenyldiazomethane indicate there is a considerable amount of conjugation between the carbonyl and diazo groups, as predicted by the theoretical model.² It should be noted however, that in the theoretical model, the parameters used suggested the presence of more delocalization than was actually observed. Based on the structural parameters, for example, there is very little, if any, delocalization between the phenyl rings and either the carbonyl or the diazo group, even for ring 2 (C(9)-C(14)) which is only 17.2° out of the C(7)-C(8)-C(9)-N(1)-N(2) plane. This is not expected based on the theoretical calculations,² and, for ring 2 at least, cannot be attributed solely to

steric interactions, which would force the rings to adopt a non-planar conformation in relation to the diazoalkane backbone.

The title complex is comparable to dibenzoyldiazo-methane in many of its bonding parameters, although there appears to be more conjugation between the carbonyl and diazo groups in the monobenzoyl compound compared to the dibenzoyl compound.

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Chapter V.

The Chemistry of Dibenzoyldiazomethane with Various

Rh and Ir Complexes, and the Structure of



INTRODUCTION

Metal complexes containing the intact diazoalkane molecule are extremely rare, as outlined in Chapter I. The few such compounds which have been structurally characterized, however, show the variety of ways in which the diazoalkane molecule can coordinate to a metal centre. The aliphatic diazo molecule has been shown to coordinate end-on, through the terminal nitrogen atom;^{1,2} side-on, through both nitrogen atoms;³ through the diazo carbon atom, as a metallated diazoalkane;^{4,5} and bridging two or more metal centres.^{6,7} One of the reasons for the paucity of metal-diazoalkane complexes, with the diazoalkane ligand intact, is the reactivity of the diazo group.⁸ The diazoketone compounds, $(\text{PhCO})_2\text{CN}_2$ and PhCOCN_2Ph , described in Chapters III and IV, are of interest in this regard, since they are relatively stable molecules owing to π -delocalization through the α -ketone groups within both molecules. As such, it was hoped that reaction of these diazoketones with metal complexes would result in complexes having the diazoalkane function intact and bonded to the metal centre. Both diazoketone molecules may coordinate to a metal complex in

a variety of ways, in addition to the four bonding modes already observed in diazoalkane complexes (*vide supra*). They can be bound through the carbonyl groups alone, or chelating through the carbonyl groups and the diazo functions. In addition they can also undergo N_2 loss, resulting in the formation of carbenes, which may then be followed by ligand rearrangement as in other diazoalkane reactions.⁹ The chemistry of dibenzoyldiazomethane with several rhodium and iridium complexes was therefore investigated in order to characterize some of the potentially interesting chemistry of this molecule.

EXPERIMENTAL

All manipulations were normally carried out under an atmosphere of dinitrogen and all solvents were dried and degassed prior to use. $IrCl_3 \cdot H_2O$ and $RhCl_3 \cdot 3H_2O$ were purchased from Research Organic/Inorganic Chemical Corporation; triisopropylphosphine was purchased from Strem Chemicals, and triphenylphosphine (Aldrich Chemicals) was recrystallized from ethanol prior to use. All other chemicals were reagent grade and used as obtained. Infrared spectra were recorded on either a Perkin Elmer Model 467 spectrometer using Nujol mulls on KBr plates; or a Nicolet 7199 F.T. interferometer using a CH_2Cl_2 film cast on KBr plates. NMR spectra were recorded on a Bruker HFX-90 NMR spectrometer. Microanalysis were performed by Canadian Microanalytical Service Ltd., Vancouver.

PREPARATION OF $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$

Two methods were used, a literature preparation by Collman *et al.*¹⁰ and the one described below,¹¹ which yields a product free from contaminants. $[\text{IrCl}(\text{C}_8\text{H}_{12})]_2$ ¹² (1.0 g, 1.49 mmol) was placed in a 3 necked flask flushed with $\text{N}_2(\text{g})$. 25 mL CH_2Cl_2 was added, followed by a stream of $\text{CO}(\text{g})$, at which time the solution turned black. Triphenylphosphine (1.56 g, 6.0 mmol dissolved in 25 mL of toluene) was added and the solution slowly turned red. Over two days the solution turned yellow and yielded a yellow precipitate. On addition of 30 mL of methanol, yellow crystals quickly precipitated from the remaining yellow solution. These crystals were air filtered and dried. Their infrared spectrum showed a single sharp band at 1960 cm^{-1} .

PREPARATION OF $[\text{RhCl}(\text{PPh}_3)_2]$

1.0 g of $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$ ¹³ (2.03 mmol) and 2.18 g of PPh_3 (8.31 mmol) were placed in a 3 necked flask with 50 mL toluene. The yellow solution turned salmon pink after stirring for 24 h. The precipitate was allowed to settle and the solvent removed. The product was stored under N_2 in the refrigerator at 2°C . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum¹⁴ of the product showed two species (~1:1 ratio): $[\text{RhCl}(\text{PPh}_3)_3]$ ($\delta_1 = 47.8\text{ ppm}$, doublet of triplets, $|^1J_{\text{Rh-P}}| = 191.7\text{ Hz}$,

$|^2J_{P-P}| = 38.8 \text{ Hz}$; $\delta_2 = 31.7 \text{ ppm}$, doublet of doublets,
 $|^1J_{Rh-P}| = 143.9 \text{ Hz}$, $|^2J_{P-P}| = 38.8 \text{ Hz}$) and $[RhCl(PPh_3)_2]_2$
 $(\delta = 31.3, \text{ doublet}, |^1J_{Rh-P}| = 150.2 \text{ Hz})$.

REACTION OF $[IrCl(N_2)(PPh_3)_2]$ AND $(PhCO)_2CN_2$

0.16 g of $[IrCl(N_2)(PPh_3)_2]$ ¹⁵ ($2.05 \times 10^{-1} \text{ mmol}$) and
 0.056 g of $(PhCO)_2CN_2$ ($2.2 \times 10^{-1} \text{ mmol}$) were placed in a
 3 necked round-bottom flask, and 10 mL of CH_2Cl_2 was added.
 The yellow solution turned dark green-brown immediately,
 with gas evolution. After 48 h, the solution was dark
 red-gold. This slowly lightened to yellow after two weeks.
 A yellow crystalline product (1) was isolated in varying
 yields (up to 30%) upon cooling to $2^\circ C$. The pertinent
 spectral results are: Infrared, 1954 cm^{-1} ; $^{31}P\{^1H\}$ NMR,
 $\delta = -13.4$, singlet; mass spectrum, 974 (highest peak),
 262 (base peak), 224 and 223 m/e. The $^{31}P\{^1H\}$ NMR of the
 reaction solution indicated, in addition to the resonance
 for 1, seven other unidentified species.

REACTION OF $[IrCl(CO)(PPh_3)_2]$ WITH $(PhCO)_2CN_2$

0.10 g of $[IrCl(CO)(PPh_3)_2]$ ($1.28 \times 10^{-1} \text{ mmol}$) and 0.035 g
 of the diazoalkane ($1.41 \times 10^{-1} \text{ mmol}$) were mixed as solids
 and 10 mL of toluene was added. There was no apparent
 reaction and the yellow suspension was stirred for one week.
 A yellow solid isolated at that time was found to be the
 starting iridium carbonyl complex. No reaction product was
 observed or isolated.

REACTION OF $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ WITH PPh_3 AND $(\text{PhCO})_2\text{CN}_2$

0.16 g of $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ ¹² (1.79×10^{-1} mmol), 0.248 g of PPh_3 (9.4×10^{-1} mmol) and 0.13 g of $(\text{PhCO})_2\text{CN}_2$ (5.20×10^{-1} mmol) were mixed as solids in a reaction flask and 10 mL of toluene was added. The solution turned black immediately, with the evolution of a gas. After 24 h, the solution was a dark red-gold color, and after two weeks, lightened to a yellow-red. The solution infrared and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra indicated a mixture of species. One product precipitated as gold triclinic crystals (2) after standing at room temperature for two weeks (10% yield). The infrared spectrum showed major bands at 1636, 1577 and 1546 cm^{-1} , major peaks in the mass spectrum occurred at 974 (highest), 262 (base), 201 and 183 m/e, and the density of 2 was 1.47(1) $\text{g}\cdot\text{cm}^{-3}$. Although there was insufficient material for further characterization by NMR spectra or microanalysis, an X-ray structure of (2) was carried out (*vide infra*). No other products were characterized.

REACTION OF $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ WITH PPh_3 AND $(\text{PhCO})_2\text{CN}_2$

0.15 g of $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ ¹⁶ (2.2×10^{-1} mmol), 0.315 g of PPh_3 (1.2 mmol) and 0.16 g of $(\text{PhCO})_2\text{CN}_2$ (6.4×10^{-1} mmol) were reacted in 10 mL of toluene, as for the analogous Ir reaction. The solution turned dark red immediately, with gas evolution. After several hours, the solution was orange with an orange microcrystalline precipitate.

pitate (3). The isolated solid had infrared bands at 1675, 1625 and 1605 cm^{-1} , a singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 23.3 ppm, major peaks in the mass spectrum at 446 (highest), 262, 224, 223 and 105 (base) m/e and a melting point of 138°C. The elemental analysis of the orange product was consistent with the formulation $(\text{Ph}_3)\text{PN}_2\text{C}(\text{COPh})_2$. Analysis: calcd. for $\text{P}_1\text{O}_2\text{N}_2\text{C}_{33}\text{H}_{25}$, 6.05% P, 6.25% O, 5.47% N, 77.34% C, 4.88% H; found 6.38% P, 6.20% O, 5.45% N, 77.25% C, 4.85% H. If the orange solution was allowed to sit at room temperature for several weeks, a white crystalline material (4) appeared, in small quantities. This compound showed a singlet in the ^{31}P NMR at 18.2 ppm; infrared bands at 1610, 1590, 1580 and 1530 cm^{-1} , major peaks in the mass spectrum at 484 (parent peak), 277 and 91 (base peak) m/e, and a melting point of 185°C.

REACTION OF $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ WITH $\text{P}(i\text{-C}_3\text{H}_7)_3$ AND $(\text{PhCO})_2\text{CN}_2$

0.10 g of the Ir complex, (1.12×10^{-1} mmol) was dissolved in 10 mL toluene and 0.18 g of the phosphine (1.12 mmol) was added. After 2 h, 0.075 g of the diazoalkane (3.0×10^{-1} mmol) was introduced through a sidearm attachment, and the orange solution turned a dark red-yellow with gas evolution. After standing for several weeks, a yellow crystalline product (5) was isolated, which had peaks in the infrared spectrum at 1675, 1610, 1600 and 1575 cm^{-1} ; a singlet, ($\delta = 51.2$ ppm) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum; and

major peaks in the mass spectrum at 326 (highest), 325 (base), 160 and 105 m/e; a density of 1.178 g/ml; and a melting point of 108°C. Element analysis agreed with the formulation $(i\text{-C}_3\text{H}_7)_3\text{P}=\text{N}_2\text{C}(\text{COPh})_2$. Analysis: calcd. for $\text{P}_1\text{O}_2\text{N}_2\text{C}_{24}\text{H}_{31}$, 7.80% O, 6.83% N, 70.24% C, 7.56% H; found 7.52% O, 6.84% N, 70.09% C, 7.80% H.

REACTION OF $[\text{RhCl}(\text{PPh}_3)]_2$ AND $[\text{RhCl}(\text{PPh}_3)_3]$ WITH $(\text{PhCO})_2\text{CN}_2$

0.10 g of the mixture of $[\text{RhCl}(\text{PPh}_3)_2]_2$ and $[\text{RhCl}(\text{PPh}_3)_3]$ and 0.41 g $(\text{PhCO})_2\text{CN}_2$ (1.64×10^{-1} mmol) were mixed together and 10 mL CH_2Cl_2 was added. The solution immediately turned dark red-orange, and then became light orange with slow gas evolution, over a few minutes. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the solution indicated initially the presence of two new species ($\delta_1 = 24.8$ ppm, doublet, $|^1J_{\text{Rh-P}}| = 117$ Hz; $\delta_2 = 18.2$ ppm, singlet) along with $[\text{RhCl}(\text{PPh}_3)_2]_2$ ($\delta = 31.3$, doublet, $|^1J_{\text{Rh-P}}| = 150.3$ Hz). After 24 h, only the singlet and $[\text{RhCl}(\text{PPh}_3)_2]_2$ resonances were observed.

X-RAY DATA COLLECTION

A crystal of 2 was mounted on a glass fibre. Preliminary film data showed Laue symmetry $\bar{1}$, with no systematic absences, consistent with the space groups P1 and $\text{P}\bar{1}$. The space group was determined to be P1 as was verified by the successful refinement of the structure with acceptable positional parameters, thermal parameters and agreement indices, and by the location of all phenyl hydrogens in

electron density difference maps. A cell reduction¹⁷ failed to show the presence of higher symmetry. The reduced cell parameters along with the pertinent details of the crystal data and intensity collection are listed in Table 20. Otherwise, the data collection proceeded as described in Chapter II.

STRUCTURE SOLUTION AND REFINEMENT

The Patterson map was consistent with both space groups $P1$ and $P\bar{1}$, with one iridium atom per cell, since there were no Ir-Ir vectors apart from the origin peak. In the space group $P\bar{1}$ with $Z=1$, the iridium atom is fixed at an inversion centre, and the molecule has crystallographically imposed inversion symmetry. For the space group $P1$, the position of the iridium atom can be arbitrarily fixed. The iridium atom was therefore placed at the origin (0,0,0) to be consistent with both space group possibilities. The electron density difference map phased on the iridium position, when carefully inspected, showed two triphenylphosphine groups which were not inversion related, and superimposed upon these were the inversion related images. This confirmed that the space group was the non-centrosymmetric choice $P1$. After fixing the positions of the two pseudo-trans PPh_3 groups, all subsequent atom positions were chosen such that they were consistent with this solution. In most instances the choice between the real atom position

Table 20. Summary of Data and Intensity Collection for



Compound	[IrCl(C ₆ H ₄ COCC(C ₆ H ₅)OP(C ₆ H ₅) ₂) - (P(C ₆ H ₅) ₃) ₂] · C ₆ H ₅ CH ₃			
Formula	C ₇₀ H ₅₇ O ₂ P ₃ Cl ₁ Ir ₁			
Formula Weight	1250.81			
Cell Parameters				
a	12.1972(8)	°		Å
b	10.1629(10)	°		Å
c	11.7608(12)	°		Å
α	103.609(7)			
β	95.059(7)	°		
γ	96.619(7)	°		
V	1397.4	°		Å ³
Z	1			
Density	1.486 g·cm ⁻³ (calcd.) 1.47 (1) g·cm ⁻³ (exptl. by floatation)			
Space Group	C ₁ ¹ - P ₁			
Crystal Dimensions	0.375 x 0.135 x 0.259 mm			
Crystal Volume	0.0106 mm ³			
Crystal Faces (and Distances from an arbitrary origin within the crystal (mm))	0	0	$\bar{1}$	0.135
	0	0	1	0.115
	$\bar{1}$	0	0	0.185
	1	0	0	0.185
	0	$\bar{1}$	0	0.065
	0	1	0	0.065
	0	1	$\bar{1}$	0.110
	$\bar{1}$	0	1	0.120
Temperature	20°C			
Radiation	Cu Kα (λ = 1.540562 Å)			
μ	61.672 cm ⁻¹			
Range in Absorption Correction Factors	0.256 - 0.499			
Receiving Aperture	4mm x 4mm; 30 cm from the crystal			

Table 20, continued

Takeoff Angle	3.5°
Scan Speed	2° in 20/min
Scan Range	0.90° below $K\alpha_1$ to 0.90° above $K\alpha_2$
Background Counting Time	10 s ($3^\circ < 2\theta < 102^\circ$); 20 s (102° $\leq 2\theta \leq 120^\circ$)
2 θ Limits	3.0 - 120.0°
2 θ Limits for Centered Reflections	$45^\circ \leq 2\theta \leq 65^\circ$
Final Number of Variables	266
Unique Data Collected	4393
Unique Data Used ($F_O^2 \geq 3\sigma(F_O^2)$)	4387
Error in Observation of Unit Weight	1.378
R	0.028
R_w	0.038

and the inversion related image was unambiguous, since only the real position resulted in reasonable non-bonded contacts. In the final electron density difference maps, all hydrogen atoms except those of the toluene methyl group were unambiguously located.

Anomalous dispersion terms¹⁸ for Ir, P and Cl were included in F_C . Full matrix least-squares refinement techniques were used, with atomic scattering factors from Cromer and Waber¹⁹ for all atoms except hydrogen, for which the values from Stewart, Davidson and Simpson²⁰ were used. All phenyl carbons except those of the orthometallated ring were refined as rigid groups having D_{6h} symmetry and C-C distances of 1.392 Å. The non-group, non-hydrogen atoms were refined as individual anisotropic atoms, with the exception of the toluene methyl carbon atom, which was refined as an isotropic atom. All hydrogens, except for the methyl hydrogens of the toluene molecule, were included as fixed contributions and were not refined. Absorption corrections were applied as noted in Table 20.

Since the space group $P1$ is polar and the iridium atom has a large anomalous dispersion with Cu $K\alpha$ radiation, the correct enantiomer must be determined to avoid polar dispersion errors, which would result in significant shifts in the positions of the Ir, P and Cl atoms relative to the lighter atoms and to each other.²¹ A least squares refinement of the first model after location of all non-

hydrogen atoms converged to crystallographic residuals of $R = 0.067$ and $R_w = 0.097$, whereas the enantiomeric solution converged to $R = 0.045$ and $R_w = 0.061$. Since the latter model was significantly better than the initial one, it was assumed to be the correct enantiomer, and this model was used in all subsequent calculations. In agreement with this choice, the correct enantiomer showed a much narrower range in chemically equivalent Ir-P and P-C distances for the two triphenylphosphine groups ($2.382(2) - 2.382(3)\text{\AA}$ and $1.835(6) - 1.861(6)\text{\AA}$, respectively) than was observed for the other enantiomer ($2.333(3) - 2.428(3)\text{\AA}$ and $1.833(6) - 1.873(6)\text{\AA}$, respectively).

In the final electron density difference map, the top twenty residuals ($0.77-0.38\text{ e/\AA}^3$) were located around the toluene of solvation, the iridium atom and the phenyl rings within the molecule. In earlier difference maps, a typical carbon atom had an electron density of *ca.* 3.3 e/\AA^3 . A more detailed discussion of the methods used in the structure solution and refinement is outlined in Chapter II.

RESULTS

A stereoview of the unit cell is shown in Figure 11. Four adjacent molecules are drawn in order to show some of the packing interactions. The crystallographic *a* axis runs from left to right, the *b* axis is from the top of the page to the bottom, and the *c* axis goes into the page.

Figure 12 presents the numbering scheme used within the molecule; the carbon atoms within the phosphorus phenyl rings are numbered with 3 digits, the first represents the phosphorus atom number, the second indicates the ring number, and the third digit represents the carbon atom within the ring; the phenyl hydrogens have the same numbering scheme as their attached carbon atom. The equatorial plane, which includes the ligand of interest, is shown in Figure 13 along with some relevant bond lengths and angles. The final positional and thermal parameters for the non-group and group atoms are presented in Tables 21 and 22, respectively. The idealized positional and thermal parameters for the hydrogen atoms are given in Table 23. Least squares plane calculations are presented in Table 24, while selected interatomic distances and bond angles are given in Tables 25 and 26, respectively. A listing of observed and calculated structure amplitudes is available.²²

Figure 11. Cell Packing Diagram of $[\text{IrCl}(\text{Ph}_2\text{POC}(\text{C}_6\text{H}_5)-\text{CCO}(\text{C}_6\text{H}_4))(\text{PPh}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$.

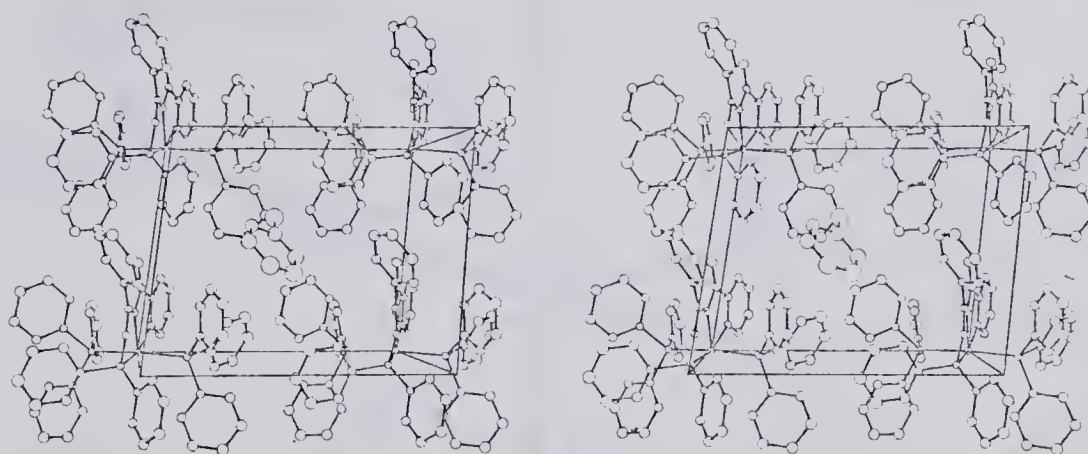


Figure 12. Perspective View of the $[\text{IrCl}(\text{Ph}_2\text{POC}(\text{C}_6\text{H}_5)\text{CCO}-(\text{C}_6\text{H}_4))(\text{PPh}_3)_2]$ Molecule.

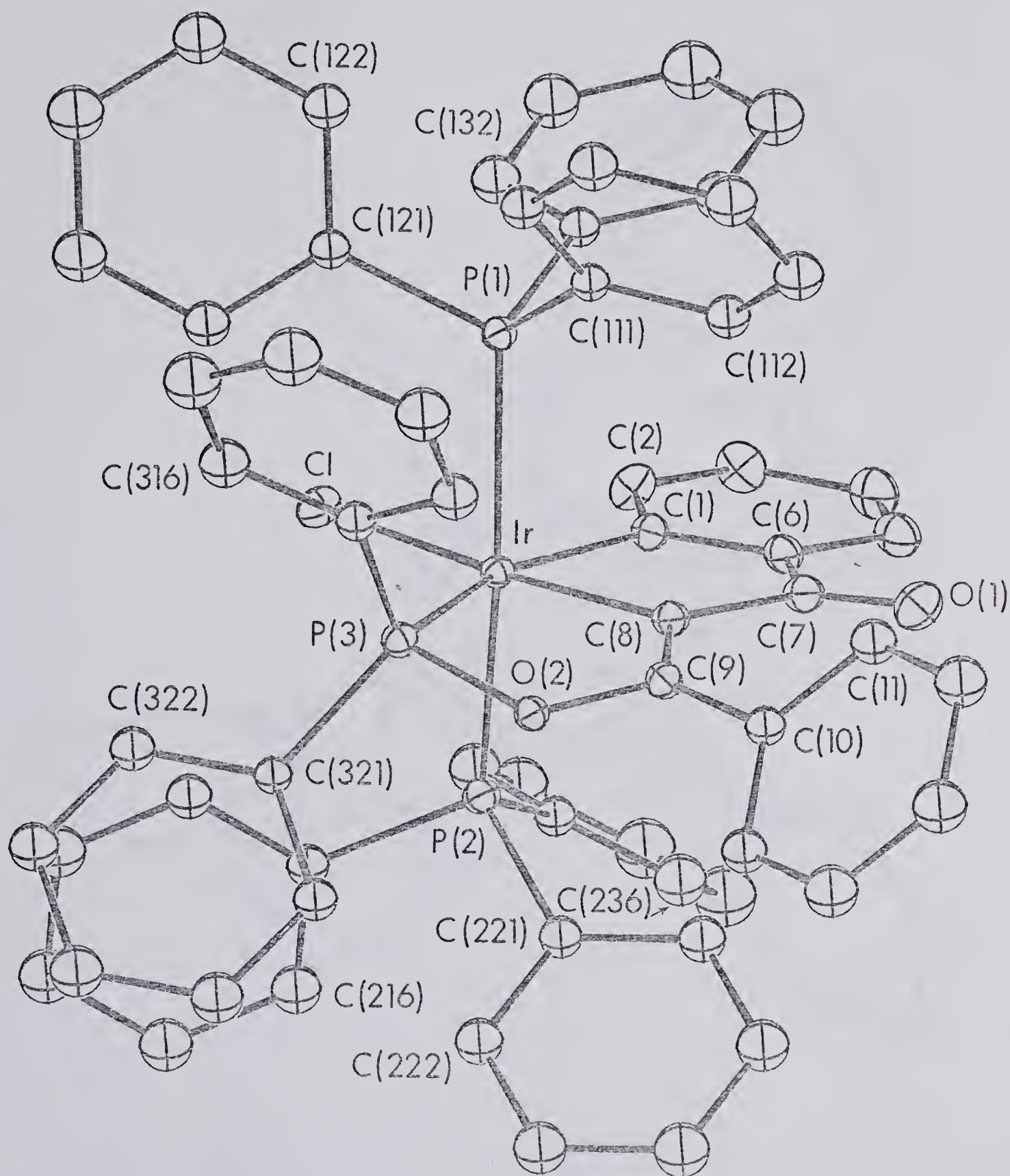


Figure 13. The Equatorial Plane of $[\text{IrCl}(\text{Ph}_2\text{POC}(\text{C}_6\text{H}_5)-\text{CCO}(\text{C}_6\text{H}_4))(\text{PPh}_3)_2]$.

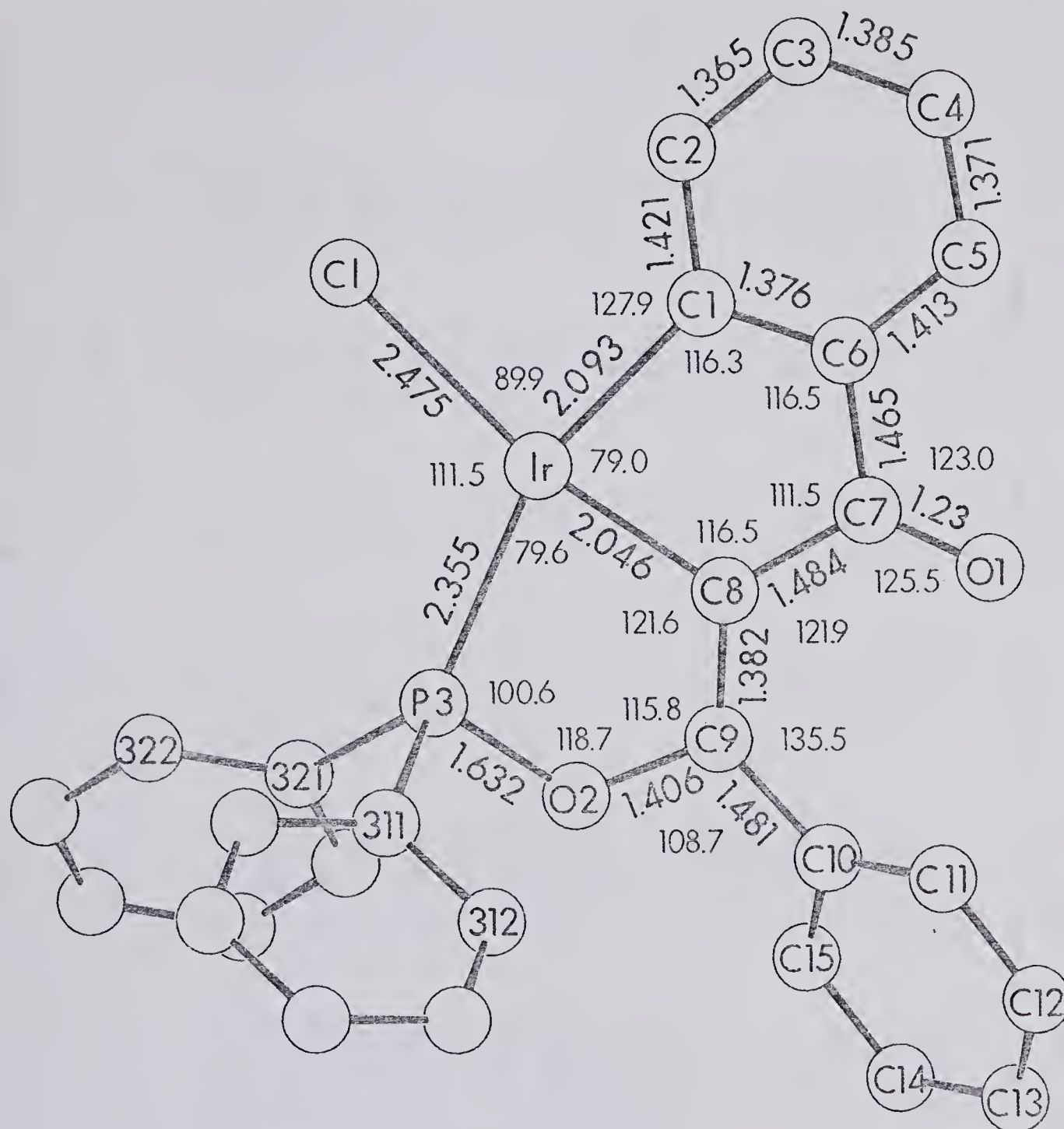


Table 21. Positional and Thermal Parameters For the Nongroup Atoms of [IrCl((C6H4)COC(Ph)OPPH2)(PPh3)2].

Atom	^a			Z	^b						
	X	Y			U11	U22	U33	U12	U13	U23	
Ir	0	0	0	0	2.57(1)	2.34(1)	2.76(1)	0.396(8)	0.300(9)	0.534(9)	
P(1)	-0.1780(2)	0.0017(3)		0.0689(2)	2.8(1)	2.9(1)	3.0(1)	0.49(8)	0.43(9)	0.64(9)	
P(2)	0.1903(2)	0.0211(3)		-0.0328(2)	2.9(1)	3.2(1)	3.6(1)	0.48(8)	0.5(1)	0.6(1)	
P(3)	-0.0594(2)	0.0471(2)		-0.1804(2)	3.3(1)	2.67(10)	3.2(1)	0.46(8)	0.41(9)	0.73(9)	
Cl	0.0536(2)	0.2124(2)		0.1584(2)	4.4(1)	3.4(1)	4.1(1)	0.08(8)	0.0(1)	-0.4(1)	
C(8)	-0.0343(7)	-0.1940(9)		-0.1064(8)	3.2(4)	2.9(4)	3.6(5)	0.8(3)	0.8(4)	1.2(4)	
O(2)	-0.0563(5)	-0.1006(5)		-0.2714(4)	5.6(3)	2.4(2)	3.0(2)	0.6(2)	0.4(2)	0.8(2)	
C(9)	-0.0599(7)	-0.2177(8)		-0.2269(8)	3.9(4)	3.0(4)	3.3(4)	0.5(3)	0.6(4)	0.7(3)	
O(1)	-0.0456(7)	-0.4293(5)		-0.0957(5)	10.0(5)	2.4(3)	5.6(3)	1.1(3)	0.4(3)	1.0(2)	
C(7)	-0.0207(6)	-0.3070(8)		-0.0484(7)	3.8(4)	3.8(4)	4.2(4)	1.3(3)	1.1(3)	1.6(3)	
C(6)	0.0281(6)	-0.2549(8)		0.0747(7)	3.7(4)	3.7(4)	4.2(4)	1.0(3)	1.0(3)	1.9(3)	
C(1)	0.0414(6)	-0.1154(9)		0.1191(7)	3.2(4)	3.8(4)	3.4(4)	1.1(3)	0.5(3)	1.1(3)	
C(2)	0.0838(8)	-0.067(1)		0.2402(8)	6.0(6)	5.4(5)	2.9(4)	0.8(4)	-0.5(4)	0.4(4)	
C(3)	0.1103(8)	-0.154(1)		0.3082(7)	6.3(6)	7.0(6)	3.6(4)	1.0(5)	-0.7(4)	2.1(4)	
C(4)	0.0975(8)	-0.293(1)		0.2596(8)	6.4(6)	6.7(6)	5.3(5)	1.8(5)	0.6(4)	3.3(4)	
C(5)	0.0552(8)	-0.3459(9)		0.1436(8)	5.4(5)	4.6(5)	6.3(5)	1.3(4)	0.8(4)	2.8(4)	
C(27)	-0.576(2)	-0.640(3)		-0.418(2)	10.1(5) ^c						

^a

Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

^bThe form of the thermal ellipsoid is: $\exp[-2^*PI^2(a^*^2U11h^2+b^*^2U22k^2+c^*^2U33l^2+2a^*b^*U12hk+2a^*c^*U13hl+2b^*c^*U23kl)]$. The quantities given in the table are the thermal coefficients $\times 10^3$. Isotropic $B(A^2)$.

Table 22. Derived Parameters For the Rigid Group Atoms of [IrCl((C6H4)COCC(Ph)OPPh2)(PPh3)2]•C6H5CH3.

Atom	x	y	z	B(A ²)	Atom	x	y	z	B(A ²)
C(21)	-0.575(1)	-0.563(1)	-0.507(1)	8.0(3)	C(121)	-0.2314(5)	0.1677(4)	0.1008(5)	3.0(1)
C(22)	-0.4926(9)	-0.459(1)	-0.5136(8)	9.7(5)	C(122)	-0.3250(5)	0.1785(4)	0.1602(5)	3.8(1)
C(23)	-0.504(1)	-0.391(1)	-0.603(1)	11.3(6)	C(123)	-0.3667(4)	0.3026(5)	0.1879(4)	4.9(2)
C(24)	-0.599(1)	-0.426(1)	-0.685(1)	12.2(7)	C(124)	-0.3148(5)	0.4157(4)	0.1563(5)	5.5(2)
C(25)	-0.6813(9)	-0.529(1)	-0.6785(8)	8.6(4)	C(125)	-0.2212(5)	0.4049(4)	0.0969(5)	5.0(2)
C(26)	-0.670(1)	-0.598(1)	-0.590(1)	6.8(3)	C(126)	-0.1795(4)	0.2809(5)	0.0691(4)	3.8(2)
C(10)	-0.0890(5)	-0.3404(5)	-0.3266(6)	3.0(1)	C(131)	-0.1818(7)	-0.0419(6)	0.2115(4)	3.0(1)
C(11)	-0.1678(5)	-0.4483(6)	-0.3207(4)	3.8(1)	C(132)	-0.1536(6)	0.0641(5)	0.3129(5)	4.4(2)
C(12)	-0.2007(5)	-0.5572(5)	-0.4190(5)	5.0(2)	C(133)	-0.1525(6)	0.0363(5)	0.4234(5)	5.5(2)
C(13)	-0.1547(5)	-0.5582(5)	-0.5234(6)	5.3(2)	C(134)	-0.1795(7)	-0.0974(6)	0.4324(4)	6.4(2)
C(14)	-0.0758(5)	-0.4503(6)	-0.5293(4)	5.1(2)	C(135)	-0.2077(6)	-0.2033(5)	0.3311(5)	6.0(2)
C(15)	-0.0430(5)	-0.3414(5)	-0.4310(5)	3.7(1)	C(136)	-0.2088(6)	-0.1756(5)	0.2206(5)	4.3(2)
C(311)	-0.2042(4)	0.0674(6)	-0.2281(4)	2.9(1)	C(211)	0.2591(4)	0.1920(4)	-0.0336(5)	3.2(1)
C(312)	-0.2755(5)	-0.0476(5)	-0.2934(6)	3.9(2)	C(212)	0.1995(3)	0.3014(6)	-0.0300(3)	3.7(1)
C(313)	-0.3827(4)	-0.0348(5)	-0.3364(5)	5.4(2)	C(213)	0.2541(4)	0.4291(5)	-0.0312(5)	5.0(2)
C(314)	-0.4187(4)	0.0929(6)	-0.3142(4)	6.3(2)	C(214)	0.3683(4)	0.4473(4)	-0.0360(5)	5.4(2)
C(315)	-0.3473(5)	0.2079(5)	-0.2489(6)	6.0(2)	C(215)	0.4279(3)	0.3378(6)	-0.0396(3)	5.1(2)
C(316)	-0.2401(4)	0.1951(5)	-0.2058(5)	4.4(2)	C(216)	0.3733(4)	0.2102(5)	-0.0384(5)	4.4(2)
C(321)	0.0134(5)	0.1535(5)	-0.2642(3)	2.6(1)	C(221)	0.2226(6)	-0.0858(5)	-0.1744(4)	3.3(1)
C(322)	0.0132(5)	0.2944(5)	-0.2335(4)	3.6(1)	C(222)	0.2642(6)	-0.0249(4)	-0.2590(5)	4.1(2)
C(323)	0.0601(5)	0.3749(4)	-0.3023(5)	4.3(2)	C(223)	0.2908(6)	-0.1057(5)	-0.3631(3)	5.1(2)
C(324)	0.1072(5)	0.3146(5)	-0.4019(3)	4.9(2)	C(224)	0.2758(6)	-0.2475(5)	-0.3826(4)	5.6(2)
C(325)	0.1073(5)	0.1737(5)	-0.4326(4)	4.8(2)	C(225)	0.2341(6)	-0.3084(4)	-0.2980(5)	5.0(2)
C(326)	0.0604(5)	0.0932(4)	-0.3637(5)	3.4(1)	C(226)	0.2075(6)	-0.2276(5)	-0.1939(3)	4.0(2)
C(111)	-0.2958(4)	-0.1162(5)	-0.0261(4)	2.7(1)	C(231)	0.2876(5)	-0.0156(7)	0.0821(4)	3.1(1)
C(112)	-0.2893(4)	-0.2557(5)	-0.0582(3)	3.5(1)	C(232)	0.3164(6)	0.0877(5)	0.1851(6)	4.7(2)
C(113)	-0.3781(4)	-0.3459(4)	-0.1272(5)	4.5(2)	C(233)	0.3928(6)	0.0711(6)	0.2740(6)	5.6(2)
C(114)	-0.4733(4)	-0.2966(5)	-0.1641(4)	4.8(2)	C(234)	0.4405(5)	-0.0489(7)	0.2598(4)	6.7(3)
C(115)	-0.4798(4)	-0.1571(5)	-0.1320(3)	4.4(2)	C(235)	0.4117(6)	-0.1523(5)	0.1567(6)	6.9(3)
C(116)	-0.3910(4)	-0.0669(4)	-0.0630(5)	3.5(1)	C(236)	0.3353(6)	-0.1357(6)	0.0679(6)	5.0(2)

Table 22, continued

Rigid Group Parameters						
	a			b		
	Xc	Yc	Zc	Delta	Epsilon	Eta
Ring1	-0.5870(7)	-0.4944(8)	-0.5961(7)	3.982(8)	2.39(1)	2.30(1)
Ring2	-0.1218(3)	-0.4493(4)	-0.4250(3)	0.624(4)	1.115(5)	2.016(4)
Ring3	-0.3114(3)	0.0802(4)	-0.2711(3)	-0.105(4)	2.802(4)	3.367(3)
Ring4	0.0603(3)	0.2341(4)	-0.3330(3)	3.149(4)	1.083(4)	2.602(3)
Ring5	-0.3846(3)	-0.2064(4)	-0.0951(3)	-0.056(4)	2.738(3)	2.581(3)
Ring6	-0.2731(3)	0.2917(4)	0.1285(3)	2.959(4)	0.638(4)	1.243(3)
Ring7	-0.1806(4)	-0.0696(4)	0.3220(4)	0.271(4)	1.637(4)	0.207(3)
Ring8	0.3137(3)	0.3196(4)	-0.0348(3)	2.917(4)	0.163(4)	2.106(3)
Ring9	0.2492(3)	-0.1667(4)	-0.2785(3)	3.232(4)	1.208(4)	3.796(3)
Ring10	0.3640(4)	-0.0323(5)	0.1709(4)	-0.310(4)	2.243(5)	0.224(4)

a

Xc, Yc and Zc are the fractional coordinates of the centroid of the rigid group.

b

The rigid group orientation angles Delta, Epsilon and Eta (radians) are the angles by which the rigid body is rotated with respect to a set of axes X, Y and Z. The origin is the centre of the ring; X is parallel to a*, Z is parallel to c and Y is parallel to the line defined by the intersection of the plane containing a* and b* with the plane containing b and c.

Table 23. Idealized Positional and Thermal Parameters For the Hydrogen Atoms of
 $[\text{IrCl}((\text{C}_6\text{H}_4)\text{COCC}(\text{Ph})\text{OPh}_2)(\text{pPh}_3)_2]\cdot\text{C}_6\text{H}_5\text{CH}_3$.

Atom	x	y	z	B(A ²)	Atom	x	y	z	B(A ²)
H(2)	0.0936	0.0279	0.2752	4.95	H(125)	-0.1857	0.4822	0.0751	5.98
H(3)	0.1381	-0.1170	0.3891	5.37	H(126)	-0.1156	0.2735	0.0284	4.80
H(4)	0.1175	-0.3531	0.3068	5.52	H(132)	-0.1350	0.1553	0.3066	5.38
H(5)	0.0444	-0.4420	0.1101	5.06	H(133)	-0.1329	0.1038	0.4925	6.49
H(11)	-0.1991	-0.4475	-0.2495	4.76	H(133)	-0.1785	-0.1161	0.5079	7.40
H(12)	-0.2543	-0.6308	-0.4150	5.99	H(135)	-0.2261	-0.2944	0.3374	6.94
H(13)	-0.1769	-0.6324	-0.5905	6.29	H(136)	-0.2282	-0.2479	0.1515	5.35
H(14)	-0.0443	-0.4508	-0.6006	6.13	H(212)	0.1217	0.2892	-0.0269	4.69
H(15)	0.0109	-0.2675	-0.4351	4.67	H(213)	0.2135	0.5039	-0.0290	6.02
H(312)	-0.2509	-0.1349	-0.3084	4.94	H(214)	0.4057	0.5345	-0.0371	6.42
H(313)	-0.4313	-0.1136	-0.3810	6.37	H(215)	0.5060	0.3503	-0.0431	6.18
H(314)	-0.4918	0.1013	-0.3439	7.29	H(216)	0.4141	0.1356	-0.0410	5.40
H(315)	-0.3719	0.2949	-0.2343	6.95	H(222)	0.2746	0.0716	-0.2457	5.09
H(316)	-0.1914	0.2736	-0.1617	5.41	H(223)	0.3193	-0.0645	-0.4208	6.10
H(322)	-0.0189	0.3357	-0.1656	4.59	H(224)	0.2938	-0.3030	-0.4536	6.64
H(323)	0.0601	0.4711	-0.2814	5.36	H(225)	0.2236	-0.4053	-0.3113	6.00
H(324)	0.1392	0.3695	-0.4489	5.90	H(226)	0.1789	-0.2692	-0.1361	4.96
H(325)	0.1393	0.1325	-0.5006	5.86	H(232)	0.2838	0.1695	0.1950	5.71
H(326)	0.0603	-0.0030	-0.3848	4.42	H(233)	0.4125	0.1417	0.3445	6.61
H(112)	-0.2243	-0.2894	-0.0330	4.52	H(234)	0.4928	-0.0601	0.3207	7.66
H(113)	-0.3737	-0.4411	-0.1491	5.48	H(235)	0.4444	-0.2341	0.1473	7.82
H(114)	-0.5340	-0.3581	-0.2111	5.83	H(236)	0.3157	-0.2063	-0.0023	5.98
H(115)	-0.5449	-0.1234	-0.1570	5.42	H(22)	-0.4285	-0.4392	-0.4541	11.66
H(116)	-0.3955	0.0283	-0.0409	4.50	H(23)	-0.4449	-0.3211	-0.6021	12.63
H(122)	-0.3603	0.1014	0.1819	4.83	H(24)	-0.6022	-0.3770	-0.7427	14.21
H(123)	-0.4304	0.3101	0.2286	5.86	H(25)	-0.7430	-0.5511	-0.7354	9.86
H(124)	-0.3432	0.5005	0.1752	6.54	H(26)	-0.7266	-0.6692	-0.5875	8.31

Table 24. Least Squares Plane Calculations.^a

plane no.	equation					
1	$-0.1670X + 0.9519Y - 0.2568Z - 0.000 = 0$					
2	$0.9523X + 0.1483Y - 0.2667Z - 0.000 = 0$					
3	$0.9672X + 0.1428Y - 0.2102Z - 0.000 = 0$					
4	$0.9576X + 0.1401Y - 0.2518Z + 0.0625 = 0$					
5	$0.9636X + 0.1062Y - 0.2453Z - 0.0120 = 0$					
6	$0.9844X + 0.1281Y - 0.1203Z + 0.0814 = 0$					

Deviations from the Planes (\AA)						
Plane no.						
Atom	1	2	3	4	5	6
Ir	0.00	0.00	0.00		-0.012	0.084
P(1)	0.00					
P(2)	0.00					
P(3)			0.00			-0.125(2)
Cl		0.00			-0.042(3) ^b	0.321(3) ^b
C(8)		0.00			0.031(9)	-0.062(9)
O(2)						0.143(6)
C(9)						-0.040(8)
O(1)					-0.131(8) ^b	
C(7)				-0.063(8) ^b	-0.039(8)	
C(6)				-0.002(8)	0.027(8)	
C(1)			0.00	0.005(8)	-0.006(8)	
C(2)				-0.001(10)		
C(3)				-0.007(10)		
C(4)				0.010(10)		
C(5)				-0.005(9)		

Dihedral Angles Between Planes

Plane A	Plane B	angle(deg)
1	2	87.1
1	3	88.4
1	4	87.8
1	5	89.8
1	6	90.7
2	3	3.4
2	4	1.0
2	5	2.8
2	6	8.7
3	4	2.5
3	5	2.9
3	6	5.3
4	5	2.01
4	6	7.7
5	6	7.4

^aX, Y and Z are the orthogonal coordinates (\AA) with X along the a axis, Y in the (a-b) plane and Z along the c* axis.

^bNot included in the least squares plane calculation.

Table 25. Selected Interatomic Distances (\AA) in

BONDED CONTACTS

Ir-P(1)	2.384(3)	O(2)-C(9)	1.406(9)
Ir-P(2)	2.380(3)	C(9)-C(10)	1.481(9)
Ir-P(3)	2.355(2)	C(9)-C(8)	1.382(12)
Ir-Cl	2.475(2)	C(8)-C(7)	1.484(11)
Ir-C(1)	2.093(7)	C(7)-O(1)	1.227(10)
Ir-C(8)	2.046(9)	C(7)-O(1)*	1.260(10)
P(1)-C(111)	1.854(4)	C(7)-C(6)	1.465(11)
P(1)-C(121)	1.846(5)	C(6)-C(1)	1.376(12)
P(1)-C(131)	1.836(5)	C(1)-C(2)	1.421(12)
P(2)-C(211)	1.842(5)	C(2)-C(3)	1.365(14)
P(2)-C(221)	1.864(5)	C(3)-C(4)	1.385(14)
P(2)-C(231)	1.852(5)	C(4)-C(5)	1.371(14)
P(3)-C(311)	1.854(5)	C(5)-C(6)	1.413(11)
P(3)-C(321)	1.834(4)	C(21)-C(27)	1.44(3)
P(3)-O(2)	1.632(5)		

NON-BONDED CONTACTS

Cl-H(2)	2.636(3)	C(27)-H(233) ^b	3.11(3)
Cl-H(212)	2.648(3)	C(312)-H(133) ^c	2.694(6)
Cl-H(126)	2.677(3)	O(2)-C(321)	2.603(6)
Cl-C(126)	3.153(6)	C(322)-H(212)	2.677(5)
Cl-C(212)	3.188(6)	C(126)-H(316)	2.688(5)
Cl-C(1)	3.238(9)	H(316)-H(322) ^d	2.13
O(2)-H(326)	2.328(5)	H(323)-H(225) ^d	2.33
O(2)-H(312)	2.345(6)	H(112)-H(136)	2.12
C(9)-H(312)	2.737(8)	H(126)-H(316)	2.34
O(1)-H(322) ^a	2.406(6)	H(13)-H(132) ^e	2.35
C(7)-H(112)	2.530(7)	H(226)-H(236)	2.12
C(7)-H(226)	2.748(7)	H(235)-H(24) ^f	2.22

* corrected for riding motion where the second atom is riding on the first.

^aAtom is positioned at $x, -1+y, z$.

^bAtom is positioned at $-1+x, -1+y, -1+z$.

^cAtom is positioned at $x, y, -1+z$.

^dAtom is positioned at $x, 1+y, z$.

^eAtom is positioned at $x, 1+y, 1+z$.

^fAtom is positioned at $1+x, y, 1+z$.

Table 26. Selected Bond Angles (deg) in $[\text{IrCl}(\text{C}_6\text{H}_4 - \text{COCC}(\text{C}_6\text{H}_5)\text{OPPh}_2)(\text{PPh}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$.

P(1)-Ir-P(2)	169.46(8)	C(321)-P(3)-O(2)	97.2(2)
P(1)-Ir-P(3)	94.64(7)	P(3)-O(2)-C(9)	118.7(5)
P(1)-Ir-Cl	84.58(8)	O(2)-C(9)-C(8)	115.8(7)
P(1)-Ir-C(1)	88.1(2)	O(2)-C(9)-C(10)	108.7(6)
P(1)-Ir-C(8)	95.4(2)	C(10)-C(9)-C(8)	135.5(7)
P(2)-Ir-P(3)	93.18(8)	C(9)-C(8)-C(7)	121.9(8)
P(2)-Ir-Cl	85.98(9)	C(8)-C(7)-O(1)	125.5(8)
P(2)-Ir-C(1)	87.3(2)	C(8)-C(7)-C(6)	111.5(7)
P(2)-Ir-C(8)	92.9(3)	O(1)-C(7)-C(6)	123.0(7)
P(3)-Ir-Cl	111.54(8)	C(7)-C(6)-C(1)	116.5(6)
P(3)-Ir-C(1)	158.5(2)	C(7)-C(6)-C(5)	120.6(7)
P(3)-Ir-C(8)	79.6(2)	C(6)-C(1)-C(2)	115.7(7)
Cl-Ir-C(1)	89.9(3)	C(1)-C(2)-C(3)	122.3(8)
Cl-Ir-C(8)	168.9(2)	C(2)-C(3)-C(4)	120.2(8)
C(1)-Ir-C(8)	79.0(4)	C(3)-C(4)-C(5)	120.1(7)
Ir-P(1)-C(111)	117.2(2)	C(4)-C(5)-C(6)	118.8(8)
Ir-P(1)-C(121)	116.5(2)	C(5)-C(6)-C(1)	122.8(8)
Ir-P(1)-C(131)	113.5(2)	P(1)-C(111)-C(112)	119.3(3)
Ir-P(2)-C(211)	117.6(2)	P(1)-C(111)-C(116)	120.7(3)
Ir-P(2)-C(221)	116.0(2)	P(1)-C(121)-C(122)	118.2(3)
Ir-P(2)-C(231)	115.4(2)	P(1)-C(121)-C(126)	121.8(3)
Ir-P(3)-C(311)	124.6(2)	P(1)-C(131)-C(132)	117.6(3)
Ir-P(3)-C(321)	129.7(2)	P(1)-C(131)-C(136)	122.4(3)
Ir-P(3)-O(2)	100.6(2)	P(2)-C(211)-C(212)	121.5(3)
Ir-C(8)-C(9)	121.6(6)	P(2)-C(211)-C(216)	118.5(3)
Ir-C(8)-C(7)	116.3(6)	P(2)-C(221)-C(222)	120.5(3)
Ir-C(1)-C(6)	116.3(6)	P(2)-C(221)-C(226)	119.5(3)
Ir-C(1)-C(2)	127.9(7)	P(2)-C(231)-C(232)	116.2(3)
C(111)-P(1)-C(121)	103.2(3)	P(2)-C(231)-C(236)	123.8(4)
C(111)-P(1)-C(131)	103.4(3)	P(3)-C(311)-C(312)	118.4(3)
C(121)-P(1)-C(131)	100.9(3)	P(3)-C(311)-C(316)	121.5(3)
C(211)-P(2)-C(221)	102.0(3)	P(3)-C(321)-C(322)	119.5(3)
C(211)-P(2)-C(231)	98.7(3)	P(3)-C(321)-C(326)	120.3(3)
C(221)-P(2)-C(231)	104.8(3)	C(22)-C(21)-C(27)	126(1)
C(311)-P(3)-C(321)	98.7(2)	C(26)-C(21)-C(27)	114(1)
C(311)-P(3)-O(2)	97.5(3)		

DESCRIPTION OF STRUCTURE

The unit cell of $\tilde{2}$ consists of a discrete iridium monomer and one molecule of toluene of solvation. There are two non-bonded contacts between these two molecules, which are somewhat less than the sum of their van der Waals radii.²³ These contacts are between the toluene methyl group (C27) and a triphenylphosphine hydrogen atom (H(233), 3.11(3)Å) and between a hydrogen of the toluene phenyl ring (H(24)) and another triphenylphosphine hydrogen atom (H(235), 2.22 Å). The carbon atoms within the toluene molecule (C21 - C27) have large thermal parameters, which is not unusual for such molecules of solvation.²⁴ The bond length between the phenyl ring and the methyl group (C(21)-C(27), 1.44(3)Å) is somewhat shorter than in other reported structures with a toluene of solvation, but this is probably a consequence of the poor description of this molecule as shown by the large thermal motion of this group.

Within the iridium monomer, the coordination about the metal centre is quasi-octahedral. Two triphenylphosphine groups, which are mutually trans occupy the axial positions while a chlorine atom and the unusual tridentate ligand, $((C_6H_4)COCC(C_6H_5)OPPh_2)$, occupy the equatorial sites, with the tridentate ligand coordinating through an orthometallated phenyl ring, a metallated vinylic carbon atom and a phosphorus atom. The chlorine atom is trans to the olefinic

carbon atom (C(8)), while the metallated phenyl ring (C(1)-C(6)) and the diphenylphosphine group (P(3)), are mutually trans. Coordination about the iridium atom is distorted slightly from an octahedral geometry as a result of the constraints imposed by the chelating ligand and the large bulk of the ligands. Consequently, the P(3)-Ir-C(1) angle ($158.5(2)^\circ$), and the P(3)-Ir-C(8) and C(8)-Ir-C(1) angles ($79.6(2)^\circ$ and $79.0(4)^\circ$, respectively) are significantly different than the idealized values of 180° and 90° . Furthermore, the Cl-Ir-C(8) angle is $168.9(2)^\circ$, with the chlorine atom bent away from the Ph_2P group of the tridentate ligand (P(3)-Ir-Cl = $111.54(8)^\circ$). In the axial plane, the two triphenylphosphine groups (P(1) and P(2)) are bent back away from the C(1)-C(8)-P(3) plane, with a P(1)-Ir-P(2) angle of $169.46(8)^\circ$. This forces the PPh_3 groups closer to the chlorine atom (P(1)-Ir-Cl = $84.58(8)^\circ$ and P(2)-Ir-Cl = $85.98(9)^\circ$), resulting in two close, non-bonded contacts between the hydrogens of the phenyl rings and the chlorine atom (Cl-H(212), $2.648(3)\text{\AA}$; Cl-H(126), $2.677(3)\text{\AA}$). There is also a close non-bonded contact between the chlorine atom and H(2) ($2.636(3)\text{\AA}$) of the orthometallated ring of the ligand. These contacts are significantly shorter than normal Cl-H van der Waals contacts of 3.0\AA .²³ The two PPh_3 groups are bent away from the tridentate ligand in order to minimize the steric interactions between the phenyl rings and this bulky ligand. As it is, there are still two

short non-bonded contacts between C(7) of the ligand and two hydrogen atoms from the triphenylphosphine groups (C(7)-H(112), 2.530(7)Å; C(7)-H(226), 2.748(7)Å).

The two Ir-P bond distances for the mutually trans phosphine groups (P(1), 2.384(3); and P(2), 2.380(3)Å) agree very well with each other, and are typical for this type of bond.²⁵ The Ir-P-C bond angles (average 116.0(15)°), the C-P-C bond angles (average 102.2(20)°), and the P-C bond lengths (average 1.849(9)Å) are also as expected for triphenylphosphine groups.

The Ir-Cl bond length of 2.475(2)Å is considerably longer than that found in Ir(III) complexes in which two chlorine atoms are trans to each other where values of *ca.* 2.338(2)Å are typical,²⁶ and results from the large trans influence of the σ -bound olefinic carbon atom. Analogous lengthening of the Ir-Cl bond has been observed in other octahedral iridium III complexes where the chlorine atom is trans to an sp^2 hybridized carbon atom²⁷⁻³¹ resulting in Ir-Cl distances ranging from 2.44(1) to 2.52(2)Å.

The unusual tridentate ligand in the equatorial plane has resulted from the condensation of the carbene ligand, formed from the loss of N₂ from dibenzoyldiazomethane, and a diphenylphosphine group, such that the two groups are fused at a ketonic oxygen and the phosphorus atom. This tridentate ligand is bound to the metal through the phosphorus atom and is also bimetallated at the vinylic posi-

tion of C(8) and at the orthocarbon atom, C(1), of one of the benzoyl groups, such that the resulting chelate consists of two five-membered rings adjacent to each other (see Figure 13). This iridium complex is not unlike the two Rh complexes $[\text{RhCl}((\text{C}_6\text{H}_5)\text{CONCS})_2(\text{PPh}_3)_2]^{32}$ and $[\text{RhCl}(\text{EtOCONCS})_3(\text{PPh}_3)_2]^{33}$ which contain tridentate ligands formed from the condensation of isothiocyanate molecules. The two five-membered metallocycle rings in the present complex are planar to within 0.14 \AA ($\text{Ir-P(3)-O(2)-C(9)-C(8)}$) and 0.04 \AA ($\text{Ir-C(8)-C(7)-C(6)-C(1)}$), and are inclined to each other by 7.4° , indicating that the whole ligand is essentially planar. This was also seen for the two Rh complexes, mentioned above.^{32,33} The chlorine atom is displaced 0.32 \AA from the plane of the first chelated ring, and 0.04 \AA from the second. The second chelate ring, $\text{Ir-C(8)-C(7)-C(6)-C(1)}$ is virtually planar with the orthometallated ring (C(1)-C(6)), with an angle between the two planes of 2.0° . The oxygen atom is out of the plane of the second chelate ring by 0.14 \AA .

Within the first 5-membered ring ($\text{P(3)-O(2)-C(9)-C(8)-Ir}$), the Ir-P(3) bond length ($2.355(2) \text{ \AA}$) is significantly shorter than those of the two mutually trans triphenylphosphine groups (average $2.382(2) \text{ \AA}$). This difference may reflect the difference between the phosphine groups, since the former group now contains a phosphite linkage, or may result from chelate strain, forcing the diphenylphosphine

linkage closer to the metal. The strain of the chelate linkage is evident in the coordination about P(3), which is significantly distorted from a tetrahedral geometry. Therefore the Ir-P(3)-O(2) bond angle ($100.6(2)^\circ$) is small, and the Ir-P(3)-C(311) and Ir-P(3)-C(321) bond angles ($124.6(2)$ and $129.7(6)^\circ$, respectively) are larger than in the PPh_3 groups (average $116.0(15)^\circ$). Within the PPh_2 moiety, the P(3)-C bond lengths are normal and comparable to those of the PPh_3 groups. The phosphorus-oxygen bond length, $1.632(5)\text{\AA}$ indicates a P-O single bond and is comparable to the P-O bond lengths (ranging from $1.60(1)$ to $1.63(1)\text{\AA}$) found in the orthometallated phosphite complex $[(\text{C}_8\text{H}_{14})\text{Ir}(\text{P}(\text{OC}_6\text{H}_3\text{Me})(\text{OC}_6\text{H}_4\text{Me})_2)((\text{POCH}_2)_3\text{CMe})]$,³⁴ with the P-O bond within the metallated phosphite group having a value of $1.61(1)\text{\AA}$.

Viewing the remainder of the tridentate ligand, *i.e.* that part which originated from the dibenzoyldiazomethane molecule, it is evident from the structural parameters that this group is bonded to the iridium atom as a metallated olefinic group and as an orthometallated phenyl ring. Therefore the C(8)-C(9) bond length ($1.382(12)\text{\AA}$) is close to that of a normal C=C double bond (1.34\AA),²³ and is considerably shorter than the analogous distances (average $1.473(4)\text{\AA}$) in the starting diazoalkane molecule. In contrast to this, the C(7)-C(8) distance of $1.484(11)\text{\AA}$ is typical of a C-C single bond between sp^2 hybridized carbon

atoms²³ and is comparable to the value observed in the uncomplexed diazoalkane molecule. The geometries about both C(8) and C(9) are trigonal planar, with the angles about C(8) deviating only slightly from the idealized trigonal geometry, whereas around C(9) the angles are somewhat more distorted with O(2)-C(9)-C(8), O(2)-C(9)-C(10) and C(8)-C(9)-C(10) angles of 115.8(7)°, 108.7(6)° and 135.5(7)°, respectively. This distortion, which widens the C(10)-C(9)-C(8) angle, results from the strain imposed by the Ir-P(3) distance, which is relatively long compared to the other distances within the metallocycle. Again, it is noted that this strain at C(9) opposes any further lengthening of the Ir-P(3) distance and may be responsible for this distance being shorter than the other Ir-P distances in the structure. In addition, this strain may be responsible for the deviations from planarity of this chelate ring, as O(2) is 0.143(6) Å^o above the plane and P(3) is 0.125(2) Å^o below the plane.

Also consistent with the olefinic formulation for the C(8)-C(9) bond, the C(9)-O(2) bond, 1.406(9) Å^o, is close to a normal C-O single bond (1.40 Å^o),²³ and the C(9)-C(10) distance (1.481(9) Å^o) indicates a normal C-C single bond.²³ The phenyl ring, C(10) through C(15), is skewed from the metallocycle ring by 72.5°, in order to minimize contacts with O(1) and the phenyl rings of the diphenylphosphine moiety.

Within the remainder of the tridentate ligand, the parameters are close to those in the free diazoketone (see Chapter III). Thus, C(7)-O(1) ($1.227(10)\overset{\circ}{\text{\AA}}$) is close to the uncorrected values in dibenzoyldiazomethane (average $1.223(3)\overset{\circ}{\text{\AA}}$) and indicates a bond order of two.³⁵ In addition C(6)-C(7), at $1.465(11)\overset{\circ}{\text{\AA}}$, is not significantly different from the corresponding distances in the free diazoalkane molecule (average $1.488(2)\overset{\circ}{\text{\AA}}$). The distances within the orthometallated ring, C(1)-C(6), range from $1.365(14)$ to $1.421(12)\overset{\circ}{\text{\AA}}$ and are not unusual for such a group. While the bonding parameters within the coordinated ligand are not significantly different from the uncomplexed diazoalkane molecule, the slight differences are consistent with a somewhat higher degree of delocalization within the coordinated ligand. This may result from the increased planarity of the diazoalkane molecule in the metal complex, especially between the orthometallated phenyl ring and the metallocycle ring, Ir-C(8)-C(7)-C(6)-C(1).

Both Ir-C(1) and Ir-C(8) distances ($2.093(7)$ and $2.046(9)\overset{\circ}{\text{\AA}}$, respectively) are comparable with other Ir(III) complexes in which the metal is σ -bound to an sp^2 -hybridized carbon atom (range $1.99(2)$ - $2.16\overset{\circ}{\text{\AA}}$).²⁷⁻³¹ The longer distance for the orthometallated Ir-C(1) bond in comparison to Ir-C(8) may result from the larger trans influence of P(3) compared to Cl, or it may reflect the restrictions put on C(8) by the rest of the tridentate ligand. In other tri-

dentate ligands where the central metal linkage has been a carbon atom, these metal carbon bonds have been unusually short.^{32,33,36}

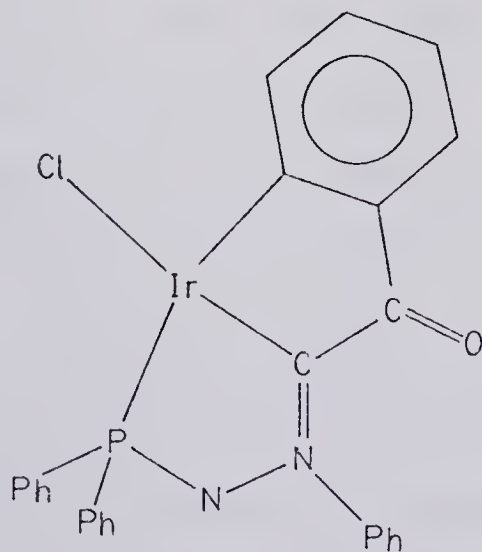
DISCUSSION

STRUCTURE OF $[\text{IrCl}((\text{C}_6\text{H}_4)\text{COCC}(\text{C}_6\text{H}_5)\text{OPPh}_2)(\text{PPh}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$

Complex 2 is rather novel in that it contains the unusual tridentate ligand, $((\text{C}_6\text{H}_4)\text{COCC}(\text{C}_6\text{H}_5)\text{OPPh}_2)$ formed from a dibenzoyl carbene fragment and a PPh_2 group. This complex was formed in the reaction of $[\text{IrCl}(\text{C}_8\text{H}_{14})]_2$ with PPh_3 and $(\text{PhCO})_2\text{CN}_2$, in which the diazoalkane ligand has lost N_2 , coordinated to the metal centre through the carbene carbon atom, and has undergone orthometallation of one of the phenyl rings. In addition one of the ketonic oxygen atoms has coordinated to a PPh_2 group, which is coordinated to the metal via the phosphorus atom. The diphenylphosphine group bonded to the ketonic oxygen (O(2)), originated, presumably, from a triphenyl phosphine group, since only PPh_3 was used in the reaction mixture. Consequently, fragmentation of PPh_3 must have occurred, with the loss of a phenyl ring. Activation of P-C bonds have been reported for various metal complexes including those of Rh and Ir,^{37,38} Ru³⁹ and Os.⁴⁰ In most cases bridging PR_2 groups result, with the third R group absent from the complex. For example, refluxing either $[\text{Ir}(\text{CO})\text{H}(\text{PPh}_3)_3]$ or $[\text{IrH}_3(\text{PPh}_3)_3]$ in DMF or decalin results in the formation of $[\text{Ir}(\text{CO})(\text{PPh}_3)_\mu-(\text{PPh}_2)]_2$,³⁸

presumably with the loss of benzene. However, in the complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}-\mu\{\text{C}(\text{Ph})\text{O}\}-\mu\{\text{C}(\text{CH}_3)\text{O}\}-\mu(\text{PPh}_2)\text{Mn}(\text{CO})_3]$,³⁷ the phenyl group migrated to a carbonyl ligand. In the present complex, there is no evidence of the fragmented phenyl ring; nor is there evidence of the hydrido ligand resulting from the orthometallation reaction. The distorted octahedral coordination about the iridium atom shows no vacant coordination site in which the hydrido ligand could be located and no electron density consistent with such a ligand was observed. Furthermore, the complex, as it is formulated, is an 18 e^- compound and cannot accommodate the extra hydride ligand. We assume therefore that at some stage, metal activation of the P-phenyl bond has occurred with reductive elimination of the phenyl group and hydride ligand as benzene. The phenyl ring fragmentation may have resulted from increased steric interactions after coordination of the diazoalkane ligand to an intermediate such as $[\text{IrCl}(\text{PPh}_3)_3]$.

Another conceivable possibility for this complex would have a dinitrogen containing fragment as presented below.



Such a species (having the PPh_3 groups above and below the plane shown) could result from attack by the diazoalkane molecule at a coordinated PPh_3 group, cleavage of one benzoyl group and migration of a phenyl group from the PPh_3 ligand to one of the nitrogen atoms. Certainly $\text{Ph}_3\text{P}-\text{NNCR}_2$ compounds resulting from the reactions of phosphines with diazoalkane molecules are well known (*vide infra*). In addition, migration of a phenyl group has been observed, as in the formation of

$[\text{Fe}_2(\text{CO})_6](\mu\text{-PPh}_2)(\mu\text{-PPh} \text{---} \overbrace{\text{C}=\text{C}(\text{CF}_2)_2(\text{CF}_2)_2}^{\text{---}} \text{C}=\text{CPh})$ from the starting ditertiary phosphine $(\text{Ph}_2\text{P} \text{---} \overbrace{\text{C}=\text{C}(\text{CF}_2)_2(\text{CF}_2)_2}^{\text{---}} \text{C}=\text{CPhPh}_2)$.⁴¹

However the observed geometry in the present structure is not as consistent with this possibility, since the nitrogen atom bound to phosphorus would be significantly displaced from the ligand plane, having a P-N-N angle which would be close to the tetrahedral value. Furthermore, we would expect a shorter C=N bond than is observed. In order to crystallographically verify that the correct solution involved a carbonyl fragment (C(9)-O(2)), and not a dinitrogen fragment, the latter model was refined to convergence. The poorly behaved thermal parameters⁴² and the poorer crystallographic residuals for the model involving nitrogen atoms ($R = 0.029$ $R_w = 0.038$), confirmed that a carbonyl fragment was involved, as shown in Figures 12 and 13.

Compound 2 can be considered as an Ir(III) complex, with the $((\text{C}_6\text{H}_4)\text{COCC}(\text{Ph})\text{OPPh}_2)$ ligand formally a dianionic

ligand, and the metallated phenyl carbon (C(1)) and the metallated C(8) atom both negatively charged. This would indicate that C(8) is not a carbene atom (which is a neutral 2 electron donor), but an unsaturated carbon atom, similar to that found in metallated phenyl rings. Consistent with this, the bond between C(8)-C(9) is a double bond, rather than a single bond as expected for a carbene atom, and C(8) is best considered as a metallated olefinic carbon atom.

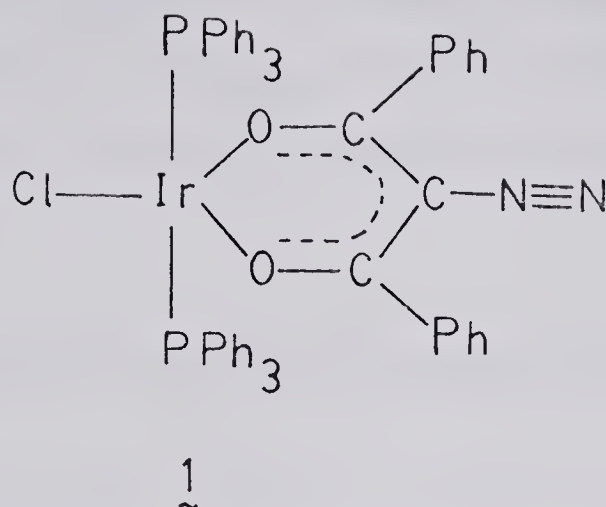
The original bonding parameters within the parent diazoalkane molecule have changed considerably upon coordination to the iridium complex. Overall, the ligand is considerably more planar than before complexation, which leads to a greater amount of electron delocalization. This is seen in the lengthened C(7)-O(1) bond and shortened C(7)-C(6) bond as compared to the free aliphatic diazo molecule. The other C-O group within the coordinated ligand is completely different from the free molecule, as the oxygen is bonded to both C(9) and P(3) rather than just one carbon atom. This in turn results in a C=C double bond between C(9)-C(8), as compared to the same bond in the free molecule, which had a bond order of *ca.* 1.5.

REACTION OF $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ AND $(\text{PhCO})_2\text{CN}_2$

The free dibenzoyldiazomethane molecule has infrared stretching frequencies of 2100 cm^{-1} for ν_{NN} and 1625, 1596

and 1575 cm^{-1} for ν_{CO} , while $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ has an NN stretching frequency of 2105 cm^{-1} .⁵ After reaction, the yellow crystalline compound (1) shows a single band above 1500, at 1954 cm^{-1} . Since the N_2 group of $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ is very labile, and is not expected to be retained during the reaction, this 1954 cm^{-1} band is assigned to ν_{NN} of the coordinated aliphatic diazo ligand. The mass spectral data of 1 support this conclusion, since the highest peak of 974 m/e (assigned to $[\text{IrCl}(\text{PPh}_3)_2(\text{PhCOCCOPh})]^+$) and the peaks at 224 and 223 m/e ($\text{PhCOCH}_2\text{COPh}^+$ and PhCOCHCOPh^+ , respectively) indicate that the ligand is indeed present. Although the diazoalkane N_2 group is not observed in the mass spectrum, this does not indicate that it is absent in (1) since the N_2 group cleavage is quite facile under the conditions used to obtain the mass spectrum. A similar N_2 cleavage was observed in the mass spectrum of the parent diazoalkane molecule. Other peaks in the mass spectrum were consistent with the assignment of the highest peak to an iridium complex (*i.e.* 938 $(\text{Ir}(\text{PPh}_3)_2(\text{C}(\text{COPh})_2)^+$; 780 $(\text{IrCl}(\text{CO})(\text{PPh}_3)_2)^+$; 751 $(\text{IrCl}(\text{PPh}_3)_2)^+$; 716 $(\text{Ir}(\text{PPh}_3)_2)^+$ and 638 m/e $(\text{Ir}(\text{PPh}_3)(\text{PPh}_2))^+$).

The CO stretching bands are not in the expected area around 1600 cm^{-1} , indicating that coordination of the ligand to the metal has greatly altered the CO bonds. Compound 1 is most likely then, a five-coordinate iridium complex, with the diazoalkane ligand chelated through the oxygen atoms.



This would be an $18 e^-$ system, with trans phosphine ligands, consistent with the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which showed a singlet. This complex is analogous to metal-acetylacetonate complexes in which the ν_{CO} bands occur below 1700 cm^{-1} .⁴³ In the infrared spectrum of 1, there were no bands below 1600 cm^{-1} which could be assigned to the CO group of the diazoalkane ligand. However, the chelated structure is the most consistent one, in view of all the data. Preliminary X-ray crystallographic work on crystals of 1 indicated twinning within the crystals, which were also of poor diffraction quality, and a structure determination was not attempted. An elemental analysis was not carried out since compound 1 was considered pure only if single crystals were obtained, and the yield of crystals of 1 from the reaction was not consistent and usually, was very low.

REACTION OF $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ WITH $(\text{PhCO})_2\text{CN}_2$

There was no apparent reaction between the diazoalkane molecule and Vaska's complex, $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$. A similar lack of reactivity was also observed between Vaska's complex and $\text{N}_2\text{C}_5\text{Cl}_4$.¹

REACTION OF $[\text{IrCl}(\text{C}_8\text{H}_{14})]_2$, PPh_3 AND $(\text{Ph}_2\text{CO})_2\text{CN}_2$

Both infrared and $^{31}\text{P}\{^1\text{H}\}$ spectra of the solution mixture indicate that there are several species present in the mixture from the outset. In addition, the reactions involved are solvent dependent, since different $^{31}\text{P}\{^1\text{H}\}$ NMR peaks were observed in the toluene and CH_2Cl_2 solutions. Only one compound was isolated pure as a solid, compound 2, which was determined to be $[\text{IrCl}((\text{C}_6\text{H}_4)\text{COCC}(\text{C}_6\text{H}_5)\text{OPPh}_2)(\text{PPh}_3)_2]$ through an X-ray structural determination (*vide supra*). The three bands in the infrared spectrum at 1636, 1577 and 1546 cm^{-1} are not unlike the ν_{CO} bands observed in the uncomplexed aliphatic diazo molecule, although in 2 these are now the result of one C=O group and a C=C group; the assignment of these bands cannot be made unambiguously. In the mass spectrum, the highest peak (974 m/e, assigned to $[\text{IrCl}(\text{PPh}_3)_2\{(\text{PhCO})_2\text{C}\}]^+$) was the same as for compound 1 and the intact molecular ion (1251 m/e) was not observed. The fragmentation patterns between the two species 1 and 2 were not the same however, with the major peaks in 2

resulting from PPh_3 (262, base peak, PPh_3^+ ; 183, $\text{PPh}(\text{C}_6\text{H}_5)^+$) and Ph_2PO^+ (201 m/e). The tridentate ligand $\{(\text{C}_6\text{H}_4)\text{COCC}-(\text{C}_6\text{H}_5)\text{OPPh}_2\}$ was not observed although the fragments, $(\text{PhCO})_2\text{CH}_2^+$ (224), $(\text{PhCO})_2\text{CH}^+$ (223) and Ph_2PO^+ (201 m/e) were evident.

REACTION OF $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ WITH PPh_3 AND $(\text{PhCO})_2\text{CN}_2$

Two products, 3 and 4, were obtained from this reaction. The infrared spectrum of 3 showed three bands at 1675, 1625 and 1605 cm^{-1} , significantly perturbed from those of the starting diazoalkane molecule. The mass spectral data showed a highest peak of 446 m/e, with no indication of the presence of a metal species, but both PPh_3 (262 m/e) and the carbene fragment from the diazoalkane molecule were present (224, $(\text{PhCO})_2\text{CH}_2^+$; 223, $(\text{PhCO})_2\text{CH}^+$; 105, base peak, $(\text{PhCO})^+$). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also indicated that 3 was not a Rh complex, since a singlet was observed in the spectrum, with no Rh-P coupling. This compound was identified through elemental analysis as $\text{Ph}_3\text{P}=\text{N}_2\text{C}(\text{COPh})_2$, a phosphazine. The formation of phosphazines is fairly common⁴⁴ and they are often used as a method of stabilizing aliphatic diazo molecules. Compound 3 has been prepared by Regitz through refluxing PPh_3 and $(\text{PhCO})_2\text{CN}_2$ in ether for one minute.⁴⁵

Complex 4, a white crystalline material, also appeared to be a metal-free species since the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum

again showed only a singlet at 18.2 ppm, with no Rh-P coupling. This compound was identified as $\text{Ph}_3\text{P}=\text{C}(\text{COPh})_2$, a phosphorous ylide, through comparison of the infrared, $^{31}\text{P}\{^1\text{H}\}$ and mass spectra with those of an authentic sample,⁴⁶ kindly prepared by Dr. L. Vande Griende. The major peaks in the mass spectrum correspond to the ions $(\text{Ph}_3\text{PC}(\text{COPh})_2)^+$ (484, parent), Ph_3PO^+ (277) and $(\text{C}_7\text{H}_7)^+$, (91 m/e, base peak). Compound 4 has previously been prepared⁴⁶ through reaction of the phosphorane ($\text{Ph}_3\text{P}=\text{CH}-\text{COPh}$) with the carboxylic anhydride $(\text{PhCOO})_2\text{O}$.

No Rh-phosphorus complexes were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction solution.

REACTION OF $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ WITH $\text{P}(\text{i-C}_3\text{H}_7)_3$ AND $(\text{PhCO})_2\text{CN}_2$

The yellow crystalline complex 5 had a parent peak in the mass spectrum of 326 m/e, which suggested that 5 was an organic compound, rather than an Ir complex. This was confirmed through elemental analysis, and 5 was identified as $(\text{i-C}_3\text{H}_7)_3\text{P}=\text{N}_2\text{C}(\text{COPh})_2$, a phosphazine compound, analogous to compound 3. The major peaks in the mass spectrum correspond to $[(\text{i-C}_3\text{H}_7)_2\text{P}=\text{N}_2\text{C}(\text{COPh})_2]^+$ (326, highest peak), $[(\text{i-C}_3\text{H}_7)\text{HP}=\text{N}_2\text{C}(\text{COPh})_2]^+$ (325, base peak), $\text{P}(\text{i-C}_3\text{H}_7)_3^+$ (160) and $(\text{PhCO})^+$ (105 m/e). The bands in the infrared spectrum are assigned as 1675 cm^{-1} , ν_{CN} ; 1610, 1600 and 1575 cm^{-1} , ν_{CO} . No iridium-containing species was isolated.

REACTION OF $[\text{RhCl}(\text{PPh}_3)_2]_2$ AND $[\text{RhCl}(\text{PPh}_3)_3]$ WITH $(\text{PhCO})_2\text{CN}_2$

Although no compounds were isolated from this reaction, the $^{31}\text{P}\{^1\text{H}\}$ NMR results are useful in determining the reaction pathway. Of the two Rh species present, $[\text{RhCl}(\text{PPh}_3)_2]_2$ and $[\text{RhCl}(\text{PPh}_3)_3]$, only the monomer reacts with the diazoalkane molecule. The dimer resonance peaks remain unchanged, even after 1 week. The monomer reacts almost instantaneously to produce a new Rh species (6) ($\delta = 24.8$ ppm, doublet, $|^1J_{\text{Rh-P}}| = 117$ Hz), with equivalent phosphines, and an organic phosphine ($\delta = 18.2$ ppm, singlet), which has the same chemical shift as compound 4, and is presumed to be $\text{Ph}_3\text{P}=\text{C}(\text{COPh})_2$. Within 24 h, all of 6 has converted into the phosphorous ylide, compound 4, and the only Rh containing species observed in the spectrum, is the dimer $[\text{RhCl}(\text{PPh}_3)_2]_2$, whose $^{31}\text{P}\{^1\text{H}\}$ NMR signal has remained unchanged.

CONCLUSIONS

The reaction between $[\text{IrCl}(\text{N}_2(\text{PPh}_3)_2)]$ and $(\text{PhCO})_2\text{CN}_2$ produced several different species, of which only one, compound 1, was isolated and characterized. This species is believed to be $[\text{IrCl}\{(\text{OCPh})_2\text{CN}_2\}(\text{PPh}_3)_2]$, in which the diazoalkane ligand is chelated through the two ketonic oxygen atoms. Tulip and Ibers⁴⁷ reported that for the synthesis of $[\text{IrClH}\{\eta^3\text{-C}_3\text{H}_4(1\text{-C}_6\text{H}_5)\}(\text{PPh}_3)_2]$, using $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ with PPh_3 to produce *in situ* the species

" $\text{IrCl}(\text{PPh}_3)_2$ " as the starting material was much more convenient than that using $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ and resulted in higher yields, shorter reaction times and cleaner products. Consequently the $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ route was used in this study, in hopes that it would again result in cleaner, more convenient reactions. However, the reaction of $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ with PPh_3 and $(\text{PhCO})_2\text{CN}_2$ was found to be even more complex than the reaction between $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ and $(\text{PhCO})_2\text{CN}_2$, as observed from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the two reaction solutions. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for the $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ reaction solution confirmed that complex 1 (-13.2 ppm) was formed by this route as well as by the reaction of $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$. However there were several other species observed in the former route which were not observed in the latter. Compound 1 was not isolated from the $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ reaction, instead only complex 2 was obtained as a pure solid, and only in small quantities. Complex 2, in contrast to the chelating diazoalkane structure of 1, contained the novel ligand $(\text{Ph}_2\text{POC}(\text{C}_6\text{H}_5)\text{CCO}(\text{C}_6\text{H}_4))$, formed through the condensation of the carbene fragment $(\text{Ph}_2\text{CO})_2\text{C}$, (which resulted from the loss of N_2 from the starting diazoalkane molecule) and a diphenylphosphine group. It is likely that this product resulted from an excess of PPh_3 in the reaction mixture, and as such we would expect that complex 2 would not be formed in the reaction of $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ with the diazoalkane molecule,

since there is no free PPh_3 present in this reaction. Unlike the reactions reported by Tulip and Ibers,⁴⁷ the above two reaction routes involving dibenzoyldiazomethane are not comparable.

In contrast to the various species produced in the reaction of $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ with PPh_3 and $(\text{PhCO})_2\text{CN}_2$, only two species, 3 and 4 were formed in the analogous reaction with $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$. Both 3 and 4 are organic phosphorus compounds, neither of which was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the iridium reaction solution. If PPh_3 and $(\text{PhCO})_2\text{CN}_2$ are reacted together, in the absence of a metal compound, only complex 3, the phosphazine $(\text{Ph}_3\text{P}=\text{N}_2\text{C}-(\text{COPh})_2)$, is formed. This suggests that the formation of 3 in the $[\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2$ reaction may be the result of an excess of triphenylphosphine, while the formation of 4, the phosphorus ylide $[\text{Ph}_3\text{P}=\text{C}(\text{COPh})_2]$, may have been catalyzed by the rhodium complex. In agreement with this, a phosphazine was not observed in the reaction of $[\text{RhCl}(\text{PPh}_3)_3]$ with $(\text{PhCO})_2\text{CN}_2$, in which there was no excess phosphine, although the phosphorus ylide 4 was observed. In fact, compound 4 resulted from an intermediate Rh species 6, which lasted for less than 24 h, and may have been a rhodium-diazoalkane complex. Overall, it appears therefore that the rhodium species catalyzed the formation of the phosphorus ylide, 4, through coordination of the diazoalkane molecule and subsequent loss of N_2 from the diazoalkane molecule, generating

the carbene which further reacts with a coordinated phosphine ligand.

The reaction of $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$ with $\text{P}(i\text{-C}_3\text{H}_7)_3$ and $(\text{PhCO})_2\text{CN}_2$ yielded only a phosphazine, compound 5, $(i\text{-C}_3\text{H}_7)_3\text{P}=\text{N}_2\text{C}(\text{COPh})_2$, which was observed after 5 days. It is not certain when compound 5 is initially formed, as the solution was not monitored earlier than this. It is not likely that this phosphazine formation is catalyzed by the presence of the iridium complex, as no similar phosphazine was observed in the analogous reaction with PPh_3 . Furthermore, a phosphorus ylide, such as was found to be catalyzed by the rhodium metal species, was not observed.

The products formed from the reaction of dibenzoyldiazomethane with various Rh and Ir complexes are quite diverse. In particular, the diazoalkane molecule reacted very differently with the iridium species than with the rhodium complexes. With the latter, when reactions were observed (surprisingly no reaction was observed for $[\text{RhCl}(\text{PPh}_3)_2]_2$), phosphorus ylides were produced, presumably *via* metal carbene intermediates. In contrast, the iridium species did not result in phosphorus ylide formation. Significantly the only carbene-like species observed in the iridium reactions, compound 2, resulted presumably, from an initial metal-carbene compound, which subsequently formed the unusual tridentate ligand described, rather than forming a phosphorus ylide. It may be that with both rhodium and

iridium species, metal-carbene complexes are formed initially, but that these subsequently react in different ways for the two metals. The only diazoalkane-containing species isolated was compound 1, an iridium complex having the diazoalkane ligand chelated through both α -ketone groups. In the presence of free phosphine, the production of phosphazine was observed; however these were not metal catalyzed and could be prepared in the absence of a metal species. Finally, we note that in the iridium reactions, only a small number of the species present were identified, owing to the complexities of the reactions. In particular the reaction in which the species " $\text{IrCl}(\text{PPh}_3)_2$ " was generated *in situ* from the cyclooctene complex, was extremely complex and surprisingly different from the analogous reaction involving $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$.

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Appendix I: Programs Used in Crystal Structure Solution,
Refinement and Analysis.

<u>Author</u>	<u>Program</u>	<u>Description</u>
Northwestern University	AGNOST	Absorption correction program using Gaussian Integration.
J.A. Ibers A.P. Gaughan	CELREF	Refines crystal alignment and cell parameters.
S.K. Dwight	DATBL	Outputs tables of posi- tion and thermal para- meters for publication.
A. Zalkin	FORDAP	Fourier summation for Patterson or Fourier maps.
P.D. Cradwick	HATOM	Calculates positions of hydrogen atoms attached to atoms which are sp^3 or sp^2 hybridized.
M.J. Bennett B. Foxman	MMMR	Calculates starting para- meters for rigid bodies and hindered rotors.
G. Germain P. Main M.M. Woolfson	MULTAN	General direct methods program.
P. Main C.T. Grainger	NORMAL	Calculates E's, does Wilson statistics. For input to MULTAN.
M.E. Pippy F.R. Ahmed	NRC-22	Calculates least-squares planes.

Appendix I, continued

<u>Author</u>	<u>Program</u>	<u>Description</u>
W. Busing H.A. Levy	ORFFE	Calculates bond lengths, angles and associated standard deviations. Modified by W.L. Brooks and M. Elder for hindered rotors and rigid bodies.
C. Johnson	ORTEP	Thermal ellipsoids plotting program.
M.J. Bennett	PMMO	Transforms raw data to intensities, applying corrections.
A.P. Gaughan	PRCNTA	Molecular weight, % composition, density, absorption coefficient calculations from formula and cell.
M. Cowie	PUBE	Sorts data according to any desired sequence of h, k or l.
R.C. Elder	PUBTAB	Prints structure factor amplitude tables, modified by S.K. Dwight for use on the page printer.
G. Germain P. Main M.M. Woolfson	RECYCL	Calculates starting phases to be input to MULTAN once a partial structure is available.

Appendix I, continued

<u>Author</u>	<u>Program</u>	<u>Description</u>
S.K. Dwight	RIGIDH	Calculated rigid body parameters for hydrogen atoms.
C.T. Prewitt	SFLS5	Structure factor calculation and least-squares refinement of parameters. Modified by B.M. Foxman and M.J. Bennett for rigid body routine, and by W.L. Hutcheon and M.J. Bennett for the hindered rotor.
S.L. Lawton	TRACERA	General Cell Reduction Program.

Appendix II: Structure Factor Amplitudes for $[\text{Cp}_2\text{W}(\text{NH}_2\text{NPh})]-$
 $[\text{BF}_4]$, $(\text{PhCOCN}_2\text{COPh})$, $(\text{PhCOCN}_2\text{Ph})$ and $[\text{IrCl}((\text{C}_8\text{H}_4)\text{COCC}-$
 $(\text{Ph})\text{OPPh}_2)(\text{PPh}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$.

(On Microfiche in Back Pocket)

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